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# TECHNOLOGY QUARTERLY

AND

## PROCEEDINGS OF THE SOCIETY OF ARTS.

VOL. XVII SEPTEMBER, 1904 No. 3

## *PROCEEDINGS OF THE SOCIETY OF ARTS.*

*FORTY-SECOND YEAR, 1903–1904.*

May 19, 1904.

THE 42d annual meeting (597th regular meeting) of the SOCIETY OF ARTS was held in Room 22, Walker Building, on Thursday evening, May 19, at eight o'clock, Colonel Hewins in the chair. One hundred and fifty persons were present.

After the minutes of the previous meeting had been read and approved, Mr. Irving W. Reynolds and Mr. Dickson Q. Brown were elected to Associate Membership in the Society.

The annual report of the Executive Committee was read and approved.

REPORT OF THE EXECUTIVE COMMITTEE PRESENTED AT THE FORTY-SECOND ANNUAL MEETING OF THE SOCIETY, MAY 19, 1904.

The first meeting of the Society for the present year was held on October 15, 1903. Fifteen meetings have been held, with an average attendance of one hundred and seventy-five.

The following papers have been read:—

1. "American Rapid Transit in the Light of European Experience." Mr. John P. Fox.
2. "Solar Evaporators: their Development and Use in Water Engineering." Capt. W. H. Jaques.

3. "Mosquitoes and Suggestions for their Extermination." Mr. Lyman W. Underwood.

4. "One Field of Twentieth Century Science." Mr. Simon Newcomb.

5. "Influence of Food Preservatives on Digestion." Dr. Herbert W. Wiley, Chief Chemist, United States Department of Agriculture.

6. "Steam Turbines." Mr. Charles Garrison, of the De Laval Steam Turbine Company.

7. "The Use of Electricity in Metallurgy." Prof. J. W. Richards, of Lehigh University.

8. "The Chemical Work of the United States Geological Survey." Dr. F. W. Clarke, Chief Chemist, United States Geological Survey.

9. "The Action of Radium and Ultra-Violet Light on Minerals and Precious Stones." Mr. George F. Kunz.

10. "The Preservative Treatment of Wood." Dr. S. P. Sadtler.

11. "The Measurement of the Heat of the Stars." Prof. E. F. Nichols, of Columbia University.

12. "The History and Work of the Smithsonian Institution." Dr. Cyrus Adler, Librarian, Smithsonian Institution.

13. "The Recent Conflagration in Baltimore." Prof. C. L. Norton, of the Institute.

14. "Coinage and the Precious Metals." Mr. George E. Roberts, Director of the United States Mint.

15. "Mechanical Flight." Mr. J. Emery Harriman, Jr.

At the beginning of the year the Associate Membership of the Society was three hundred and fifty-three. Of these members eight have resigned and two have died. Fourteen Associate Members have been elected, making the present membership three hundred and fifty-seven. Last year there were thirty-seven Associate Life Members, two of whom have died. During the year one Life Member has been elected. Four Associate Members have become Life Members in accordance with the By-Laws of the Society, which provides for the transfer to the list of Life Members of the names of Associate Members who have paid twenty annual assessments.

The TECHNOLOGY QUARTERLY has appeared as usual, and has contained the Proceedings of the SOCIETY OF ARTS, together with a full complement of articles contributed by various authors. Among these may be mentioned an article by Prof. A. A. Noyes, which is the first of a series that will embody a new system of qualitative chemical analysis. The September number contained an elaborate and thoughtful report on Engineering Education from the pen of that eminent engineer, Dr. E. L. Corthell, dealing chiefly with the methods and facilities for instruction to be found in the engineering schools of the principal European countries. These are compared with two schools of this country, and important conclusions are drawn as to our needs.

The Mining Department of the Institute is well represented by a number of important contributions, including three articles contributed to the new edition of the Encyclopædia Britannica, which we were able to reprint by the kind permission of the publishers. From Prof. W. O. Crosby has been received a notable series of papers on the local geology of Massachusetts, containing results of investigations made by him under the auspices of the Metropolitan Water and Sewage Board and the Charles River Dam Commission.

While several departments of the Institute are usually well represented in the QUARTERLY, there are others from which contributions are rarely received. It is much to be regretted that the TECHNOLOGY QUARTERLY cannot reflect more completely the manifold scientific activity of the Institute.

The remarkably small deficit in the account of the SOCIETY OF ARTS, as shown in the last annual report of the Treasurer of the Institute, is due in large measure to the activity

of Mr. F. H. Rand, Bursar of the Institute, who at considerable personal inconvenience and without recompense obtained for the QUARTERLY advertising contracts that reduced the net cost of publication to a marked degree. In recognition of this voluntary service, the Board of Publication at its last meeting passed a vote of thanks to Mr. Rand.

GEORGE W. BLODGETT,
EDMUND H. HEWINS,
CHARLES T. MAIN,
JAMES P. MUNROE,
A. LAWRENCE ROTCH,
} *Executive Committee.*

The report of the Nominating Committee was read, and the following named gentlemen were elected officers of the Society for the year 1904–1905. Executive Committee: George W. Blodgett, Edmund H. Hewins, Charles T. Main, James P. Munroe, and A. Lawrence Rotch. Secretary: Samuel C. Prescott. Board of Publication: W. T. Sedgwick, Dwight Porter, H. E. Clifford, Henry Fay, and R. P. Bigelow.

Mr. J. Emery Harriman, Jr., then addressed the Society on "Mechanical Flight."

A vote of thanks was tendered the speaker, and the meeting adjourned.

JAMES F. NORRIS, *Secretary.*

# *A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

By ARTHUR A. NOYES.

## PART II. — ANALYSIS OF THE TUNGSTEN GROUP.

### Introduction.

This article is a continuation of one with the same title published in the preceding volume of this Quarterly. The work upon the separation and detection of the elements whose hydroxides after heating at 120° are undissolved by nitric acid, constituting what for brevity is here designated the tungsten group,[1] has now been completed; but the method of procedure is still subject to revision as a result of information that may be gained in working out more fully the later groups, and additional test analyses covering other combinations of elements will be made as opportunity occurs. This publication is therefore to a certain extent a preliminary one.

The plan of presentation adopted in the preceding article has been adhered to, special chapters being devoted to a "Tabular Outline" of the process, to a "General Discussion" of its main features, to the detailed "Procedure and Notes," to "Test Analyses" showing the efficiency of the method, and to "Confirmatory Experiments and References," substantiating the statements made in the notes.

I desire to state that during the first part of the work connected with this group Mr. B. E. Schlesinger was associated with me, and that to him are due the working out of the main subdivisions of the group and the discovery of the method of detecting tantalum in the presence of titanium. In the latter part of the work, consisting in perfecting the scheme and especially in developing the means of detecting niobium, tungsten, and tin, I have been ably assisted by Mr. D. P. Smith and Mr. C. S. Bryan, Jr. I also wish to express my thanks to Mr. F. M. Eaton for the valuable aid he has rendered by making a large number of test analyses by the final procedure.

### Tabular Outline.

An outline of the process finally adopted is given in the table on the following page. Enclosure in brackets shows that the element may divide itself between the precipitate and filtrate at the point indicated.

[1] Called the "niobium and tungsten groups" in the preceding article.

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Residue: $SiO_2$, $TiO_2$, $Ta_2O_5$, $Nb_2O_5$, $Sb_2O_5$, [$Bi_2O_3$], $SnO_2$, [$As_2O_5$], [$P_2O_5$], $WO_3$, [$MoO_3$], etc. *Dissolve in HF, pass in $H_2S$, and filter.* (*P. 31.*)

Precipitate: [$Sb_2S_5$], [$MoS_3$], [$As_2S_5$], $Bi_2S_3$, etc. *Boil with $HNO_3$, and filter.* (*P. 32.*)

Filtrate. *Add $H_2SO_4$, and evaporate to fuming point.* (*P. 33.*)

Residual solution. *Add $NH_4OH$ and $(NH_4)_2S$, digest and filter.* (*P. 35.*)

Distillate: $SiF_4$.

Precipitate: $Ta_2O_5$, $TiO_2$, $Nb_2O_5$, [$WO_3$], [$MoO_3$]. *Warm with $H_2O_2$, and filter.* (*P. 36.*)

Filtrate: $(NH_4)_2SnS_3$, $(NH_4)_3SbS_4$, [$(NH_4)_2WS_4$], [$(NH_4)_2MoS_4$], $(NH_4)_3AsS_4$.

Residue: [$MoO_3$], [$Sb_2O_5$]. Solution: [$H_2MoO_4$], [$H_3SbO_4$], $Bi(NO_3)_3$, $H_3AsO_4$. (*P. 51.*)

Residue: $Ta_2O_5$. *Dissolve in HF, add $K_2CO_3$, evaporate, add water, and boil.* (*P. 37.*)

Solution. ORANGE COLOR, TI TEST. *Evaporate with $H_2SO_4$. To part add HCl, pour through Zn column, and add $HgCl_2$.* NO PRECIPITATE, — NB ABSENT; PRECIPITATE, — NB, W, OR MO PRESENT. *If a precipitate results, to rest of solution add $NH_4OH$, filter, fuse the precipitate with $Na_2CO_3$ and S, and add water.* (*P. 38.*)

Precipitate: $2K_2TaF_7.Ta_2O_5$. TA TEST.

Residue: $TiO_2$, $Nb_2O_5$. *Dissolve in HF, evaporate with $H_2SO_4$, dilute, pour through a Zn column, add $HgCl_2$.* (*P. 38.*)

Solution: [$Na_2WS_4$], [$Na_2MoS_4$]. *Unite, acidify with $H_2SO_4$, shake, and filter.* (*P. 39.*)

Precipitate: HgCl. NB TEST.

Precipitate: $SnS_2$, [$WS_3$], $MoS_3$, $As_2S_5$, $Sb_2S_5$. *Ignite in a current of $H_2S$ gas.* (*P. 41.*)

Filtrate: [$H_2WO_4$]. *Evaporate, ignite, fuse with $Na_2CO_3$, add $HNO_3$, and boil.* (*P. 40.*)

Sublimate: $As_2S_3$.

Residue: SnS, $Sb_2S_3$, $WS_2$, $MoS_2$. *Boil with strong HCl, and filter.* (*P. 41.*)

Solution: $SnCl_2$, $SbCl_3$. *Add $HgCl_2$.* (*P. 42.*)

Residue: $WS_2$, $MoS_2$. *Heat with $HNO_3$ and $H_2SO_4$.* (*P. 43.*)

Precipitate: HgCl. SN TEST.

Solution: $H_2MoO_4$. *Add Zn and KSCN.* (*P. 45.*) MO TEST.

Residue: $H_2WO_4$. W TEST. *Add HCL and Zn.* (*P. 44.*) W CONFIRMATORY TEST.

Precipitate: $H_2WO_4$. W TEST.

## General Discussion.

1. The residue insoluble in dilute nitric acid ordinarily contains all the tin, tungsten, tantalum, and niobium present in the substance, almost all of the antimony and titanium when these are present in even rather small quantities, much of the molybdenum and germanium when the substance contains a large quantity of them, and a greater or less proportion of many other elements, such as phosphorus, vanadium, arsenic, bismuth, selenium, tellurium, copper, iron, zirconium, which are carried down with the first named elements. (See P. 5, N. 1, 3, 4, 5.) Aside from the complications introduced by the occasional presence of these foreign elements, the difficulties involved in the separation, even sufficiently for qualitative purposes, of some of the regular elements of the group — especially of titanium, niobium, tantalum, and tungsten — have proved to be far greater than that of any other elements excepting the rare-earths. And in spite of the existence of many analyses purporting to show the percentage composition of minerals containing two or more of these elements, it seems very doubtful whether any analytical method of separation has yet been developed by which quantitative results accurate even within several per cent. can be obtained. The properties of these elements are therefore well worthy of more thoroughgoing investigation from this point of view. The reader must not, therefore, be surprised to find that the scheme here proposed for the qualitative analysis of this group is somewhat complicated, and that it is not always possible to detect by it quantities as small as one or two milligrams of some of these elements, when a large quantity of some other element is present.

2. The elements of this group are at the start present in hydrofluoric acid solution, the oxides having been treated with this solvent (P. 5) to remove silica and to separate them from any undecomposed portion of the original substance. As experiments showed that the regular elements of the group, except antimony and molybdenum, are entirely unprecipitated by hydrogen sulphide from such a solution, while some of the foreign elements, bismuth, copper, selenium, and tellurium, are completely thrown out by it, it is thought best to submit the solution first to the action of this reagent. By this operation any complications that might arise in the later procedures from the presence of these elements are at once eliminated. A large part of the arsenic, antimony, and molybdenum is also removed, and this may be added to

the main nitric acid solution, thereby making it unnecessary to test for these elements later in this group. Moreover, this treatment prevents so much molybdenum from being retained with the titanium in the ammonium sulphide precipitate, which otherwise is a rather serious difficulty when a very large quantity of this element is present. It is probable that this method, involving the use of hydrogen sulphide in hydrofluoric acid solution, can be advantageously employed also for the quantitative separation of tin and tungsten from many of the other elements ordinarily precipitated by that reagent; it is not, however, possible in this way to separate those elements from antimony, arsenic, or molybdenum, since these are not by any means completely precipitated in the presence of hydrofluoric acid. The investigation of such quantitative methods can not be included within the scope of this research; but reference will occasionally be made to those which seem promising, in the hope that their study may be undertaken by others.

3. The solution is next evaporated with sulphuric acid to remove the hydrofluoric acid and decompose any fluosilicic acid. Sulphuric acid is used rather than nitric or hydrochloric, since it holds in solution, even after dilution, moderate quantities of all the elements of these groups except tungsten. Experiments were made in the hope of accomplishing the separation and detection of tungsten at this point; but, although when present alone two milligrams give rise to a precipitate when the diluted sulphuric acid solution is allowed to stand, yet in the presence of titanium a much larger quantity remains in solution.

4. The method that naturally suggests itself for the subdivision of this group is digestion with ammonium sulphide solution, or fusion with sodium carbonate and sulphur followed by treatment with water, whereby titanium, niobium, and tantalum might be expected to remain undissolved, and tin, antimony, arsenic, tungsten, and molybdenum to pass into solution. This method is, in fact, often employed for the separation of titanium from tin and tungsten. Our experiments, like those of some previous investigators, have shown, however, that a considerable quantity of tungsten is retained in the titanium hydroxide precipitate, and that even five milligrams of it may be removed so completely from the sulphide solution that it cannot be detected in the filtrate. Nevertheless, we have found no better method of separation than this, and have therefore made it an important part of the scheme of analysis for this group. This is further justified by the fact

that the presence of tungsten in the titanium precipitate is indicated in the subsequent procedures, and that then it can, to a large extent, be separated from the titanium by fusion with sodium carbonate and sulphur, and be subsequently detected. The separation of tin from titanium by ammonium sulphide seems to be more satisfactory. Experiments on the method used by Defacqz for the separation of titanium and tungsten, consisting in fusion of the oxides with a mixture of potassium nitrate and carbonate, did not give so satisfactory results.

5. The quantitative separation in the wet way of the three elements, titanium, niobium, and tantalum, present in the ammonium sulphide precipitate, is also, we believe, still an unsolved problem, and even the qualitative detection of small quantities of niobium and tantalum in the presence of much titanium presented so many difficulties that it was for a long time feared that the attempt to accomplish it would have to be abandoned. The method usually employed for the separation of niobium from tantalum, based upon the different solubilities of the potassium fluoxyniobate and fluoxytantalate, gives satisfactory results; but experiments showed that this method of conversion into double fluorides was not available for the separation of either of these elements from a large quantity of titanium, owing to the intermediate solubility of the potassium fluotitanate. The common quantitative method of separating titanium from the other two elements, by fusing the oxides with potassium disulphate and extracting with cold water the titanium sulphate while leaving tantalum and niobium oxides undissolved, was found to be useless, since fairly large quantities of these elements also pass into solution when much titanium is present. Failure also attended attempts to separate these elements by treating their dried hydroxides with acidified hydrogen peroxide, and also by dropping an acid peroxide solution of them into a strongly ammoniacal solution of hydrogen peroxide, according to the method used by Walker for the separation of iron and titanium.

6. It was fortunately discovered, however, that an acid solution of hydrogen peroxide dissolves even large quantities of the precipitated hydroxides of niobium and titanium readily, and nearly completely, at any rate upon a repetition of the precipitation and treatment with peroxide; but that tantalum hydroxide, whether present in small or large quantity, whether alone or with much titanium, remains in large part (about one-half) undissolved by this solvent. It can therefore be detected in the residue by conversion into the insoluble potassium

fluoxytantalate. The dissolved part does not, moreover, interfere with the tests adopted for the other two elements.

7. It then remained to devise a plan for the detection of titanium and niobium. No satisfactory method of separation could be found. It was proved, indeed, when the hydrogen peroxide was reduced by sulphurous acid and the solution made alkaline by ammonium hydroxide, that the precipitated hydroxide of titanium dissolved completely on strongly acidifying the solution with hydrochloric acid, while that of niobium, when present alone, remained in large part undissolved. But when much titanium was present with the niobium, considerable quantities of the latter went completely into solution, so that the method was unsuitable.

8. The attempt to effect a separation of the two elements was then given up, and characteristic reactions which would show one in the presence of the other were sought for. The yellow color imparted to the peroxide solution is sufficiently characteristic of titanium, as neither tantalum nor niobium gives any color to it. There seems to exist, however, no color reaction given by niobium with a reagent which does not affect titanium. The idea then presented itself that the lower oxides, which are produced in the case of both elements by the action of zinc on acid solutions of the ordinary hydroxides, might possess markedly different reducing powers. This was found to be the case, for the lower oxide of titanium reduces mercuric chloride only very slowly, while that of niobium causes instantaneous reduction. Unfortunately, tungsten and molybdenum show the same behavior as niobium, and they are apt to be retained in the ammonium sulphide precipitate; but it was found possible to remove them almost completely by the fusion with sodium carbonate and sulphur above referred to, so that error from this source may be avoided. It seems probable that the power of the lower oxide of niobium of reducing mercuric chloride might be used for the quantitatative estimation of this element in the presence of tantalum and titanium perhaps best by weighing the precipitated murcurous chloride.

9. Difficulty was also met with in the isolation of the tungsten from the alkaline sulphide solution; for upon acidification a large part, or if it is present in small quantity almost the whole, of that element, remains in solution, probably in a colloidal condition. Much more tungsten is precipitated if ferric chloride is added to the acidified solution, and the mixture is shaken and allowed to stand; but to detect

small quantities of tungsten, it is even then necessary to recover it from the filtrate, so that the use of ferric chloride is not ordinarily to be recommended. The filtrate is merely evaporated, the residue ignited and fused with sodium carbonate, and the aqueous solution of it immediately tested for tungsten by acidification; so that no complications other than are involved in the performance of a few additional operations are introduced.

10. The sulphide precipitate may contain tin, antimony, tungsten, molybdenum, arsenic, and vanadium. It was found that the separation of the first two elements from any of the others (except molybdenum) by heating with concentrated hydrochloric acid was very imperfect, owing to the not inconsiderable solubility of the moist sulphides of tungsten, vanadium, and arsenic in that solvent. Fairly large quantities of tungsten especially went into solution when accompanied by a large quantity of tin, and thus escaped detection. On the other hand, the process sometimes used for the quantitative separation of tin and tungsten, which consists in igniting the sulphides in a current of hydrogen sulphide and then treating them with strong hydrochloric acid, was found to give excellent results with all the metals concerned, and was adopted as part of the procedure. Incidentally it has the advantage of volatilizing any arsenic present, which might otherwise prevent the separation of even a large quantity of tungstic acid in the later treatment of the sulphides with nitric acid.

11. The only other matter which requires mention is the separation of tungsten and molybdenum. When the latter element is absent, or present only in small quantity, tungstic acid alone separates as a yellow powder, upon treating with nitric acid the sulphides from which the antimony and tin have been previously extracted with hydrochloric acid; but if much molybdenum is present, even a considerable quantity of tungsten remains in solution, and if the solution is evaporated the molybdenum itself separates, after which it redissolves in acid with great difficulty. Some supplementary method of separation is therefore necessary. The most suitable one found is that of Ruegenberg and Smith as modified by Hommel, which consists merely in evaporating with sulphuric acid nearly to the fuming point, digesting for a time, and then diluting, whereby the tungsten is precipitated and the molybdenum retained in solution. The separation is not very sharp; yet as little as three milligrams of tungsten always precipitate, while even a large quantity of molybdenum does not do so.

## Procedure and Notes.

**Procedure 31.** — Dilute the HF solution (P. 6) of the residue insoluble in $HNO_3$ with half its volume of water, cover the dish, and pass $H_2S$ gas into the cold solution through a platinum or lead tube. [If the solution becomes dark colored without yielding a precipitate, add at once 1 ccm. $H_2SO_4$ (1.84).] Continue to pass the gas till the solution is completely saturated. Filter through a filter supported on a platinum ring, collecting the filtrate in a platinum dish. Heat the filtrate nearly to boiling, pass $H_2S$ into it for 5 minutes, and, if a precipitate forms slowly, continue to pass the gas for at least 20 minutes, and filter again. Wash the precipitate. (Precipitate, P. 32; filtrate, P. 33.)

*Notes.* — 1. No precipitation, either cold or hot, proves the absence of antimony, arsenic, and molybdenum. An orange precipitate in the cold shows antimony; a yellow one separating from the hot solution, arsenic; a brownish-black one separating from the hot solution, molybdenum.

2. From the HF solution a large part of the antimony and of the arsenic, by far the larger proportion of the molybdenum, and all of the bismuth, copper, selenium, and tellurium are precipitated. Tin and tungsten are not precipitated even when 500 mgm. are present, nor is a large proportion of either of these elements carried down, even when a small quantity (2–4 mgm.) is present together with a large quantity (300–500 mgm.) of antimony or molybdenum. Small quantities of lead (less than 6 mgm.) are not precipitated.

3. The HF should be cold at first, and so dilute as to contain not more than 6% HF, in order to secure the separation of 1 mgm. of antimony, which then occurs even in the presence of 500 mgm. of tin. Though this small quantity of this element is precipitated, a large quantity does not separate completely. The $H_2SO_4$ is added, when the coloration shows it to be necessary, to coagulate $MoS_3$, which may otherwise remain in the colloidal state and separate upon the subsequent addition of this acid as a gelatinous mass, which is difficult to filter and which carries down with it other elements; the addition of the acid, if not necessary for this reason, is undesirable, since it prevents the separation of a quantity of antimony less than 2 mgm. The solution is finally heated and again treated with $H_2S$ in order to cause the partial separation of even 1 mgm. of arsenic. The passing of the gas is continued so as to precipitate a large proportion of the arsenic, antimony, and molybdenum, when these are present in considerable quantity.

**Procedure 32.** — Heat the $H_2S$ precipitate (P. 31) with 5–10 ccm.[1] $HNO_3$ (1.20) until the sulphides are decomposed, adding some stronger $HNO_3$ (1.42) if necessary. Evaporate the solution to dryness, add $HNO_3$ (1.05), heat, and filter. (Filtrate, P. 51, uniting it with the main solution from P. 5; residue, reject.)

*Note.* — 1. The residue is treated with $HNO_3$ and the solution evaporated, so as to leave behind most of the antimony and molybdenum, the presence of which in large quantity in the main solution would somewhat increase the difficulties involved in the subsequent analysis of the $H_2S$ precipitate. The filtrate is not likely to contain any element not also present in the main $HNO_3$ solution (P. 5), but it is well to unite the two solutions as a precaution.

**Procedure 33.** — [If it is not known from previous indications whether any element of this group is present, boil the filtrate from the $H_2S$ precipitate (P. 31) till the $H_2S$ is expelled, add 1 ccm. $HNO_3$ (1.42), evaporate nearly to dryness, pour into a platinum crucible, and evaporate to complete dryness; if there is a residue, dissolve it in a little HF.]

To the filtrate from the $H_2S$ precipitate (P. 31) [or to the HF solution of the residue after its evaporation as just described] add 2–3 ccm. $H_2SO_4$ (1.84), and evaporate till the acid fumes strongly. [If the liquid is dark colored, add $HNO_3$ (1.42) and evaporate again.] Cool the solution and pour it into 5 ccm. water. (Part of solution, P. 34; remainder, P. 35.)

*Notes.* — 1. A heavy yellow or greenish-yellow residue proves the presence of tungsten; a blue coloration on the sides of the dish, that of molybdenum. The absence of these indications is inconclusive.

2. If $SiO_2$ was added to decompose fluorides (P. 3), the original residue insoluble in dilute $HNO_3$ (P. 5) may have consisted wholly of this substance, in which case it would be useless to continue the analysis of this group: hence the evaporation to dryness, in such a doubtful case, to see whether there is still a residue. Any $SiO_2$ present is volatilized as $SiF_4$. $HNO_3$ is added to avoid volatilization of $TiF_4$, $NbF_5$, and $TaF_5$ (P. 3, N. 4); and the solution, when nearly evaporated, is transferred to a crucible so that a small residue may be more certainly detected. If it is doubtful whether the quantity of the residue is important, the

[1] When, as in this case, a variable quantity of a reagent is given, it is to be understood that the quantity used is to be proportioned within the limits indicated to the amount of the precipitate or residue.

crucible had best be weighed before redissolving the residue in HF, and afterwards weighed empty.

3. The evaporation with $H_2SO_4$ serves to expel all fluorine, which would prevent complete precipitation of the hydroxides of tantalum, niobium, and titanium at the next stage of the process, and attack the porcelain vessels used in the later operations.

4. Moderate quantities of all the elements that may be present are held in solution in the cold, diluted $H_2SO_4$ except tungsten. This, if present alone in quantity as large as 2–4 mgm., separates upon dilution as a white gelatinous precipitate, or if in large amount as a heavy yellow or greenish-yellow powder, even before the $H_2SO_4$ is diluted. Niobium and tantalum, when present in large quantity, may also precipitate, especially if the liquid is allowed to become hot.

5. If much molybdenum is present, any portions of the substance on the sides of the dish above the concentrated $H_2SO_4$ solution may exhibit a deep blue color; and the diluted solution may also be deep blue, owing to partial reduction to a lower oxide. In the presence of much molybdenum, the $H_2SO_4$ solution may also be brown or black, owing to the formation of $MoS_3$ after the solution was filtered; in this case it is important to add $HNO_3$ to reoxidize the molybdenum, since otherwise it will not dissolve completely on the following treatment with $(NH_4)_2S$.

**Procedure 34.** — Filter $\frac{1}{2}$ ccm. of the $H_2SO_4$ solution (P. 33), if not clear already, add it to 5 ccm. $(NH_4)_2MoO_4$ solution, and heat the mixture to 60° or 70°. [If a precipitate results and if $H_2S$ produced a precipitate in the HF solution (P. 31), dilute another $\frac{1}{2}$ ccm. portion of the $H_2SO_4$ solution with 3 ccm. water, place it in a test tube in a steam bath, pass $H_2S$ into it slowly for 20 minutes, filter, boil the filtrate till the $H_2S$ is expelled, and add it to 5 ccm. $(NH_4)_2MoO_4$ solution.] (Precipitate and solution, reject.)

*Notes.* — 1. No precipitation proves the absence of both phosphate and arsenate. The formation of a fine yellow precipitate proves the presence of one of these radicals, and after the treatment with $H_2S$, it proves the presence of phosphate.

2. Arsenic acid, especially on heating to boiling, gives a yellow precipitate entirely similar to that (consisting of $(NH_4)_3PO_4.12MoO_3$) given by phosphoric acid. If, therefore, arsenic can be present, as shown by the formation of a precipitate with $H_2S$ in the HF solution, it must be first removed as described in the bracketed part of this procedure.

3. To insure sensitiveness in this phosphate test, it is necessary that the reagent be added in large excess, so as to diminish the solubility

of the precipitate, and that the solution be warmed, so as to promote the formation of the complex phosphomolybdic acid. Under these conditions 0.1 mgm. $PO_4$ is detected.

**Procedure 35.** — To the rest of the $H_2SO_4$ solution (P. 33) add cautiously $NH_4OH$ (0.90) till the solution becomes alkaline; then add cautiously 5–10 ccm. colorless $(NH_4)_2S$, and digest in a covered casserole at 50°–60° for 15–30 minutes, with frequent stirring. Filter, using suction if the precipitate is large, and wash thoroughly with hot water. [If the precipitate is still orange colored, return it to the casserole, heat it for 10–15 minutes with $NH_4OH$ (0.96) diluted with an equal volume of water, and filter again.] (Precipitate, P. 36; filtrate, P. 39.)

*Notes.* — 1. No precipitation with $NH_4OH$ proves the absence of tin, titanium, tantalum, and niobium; none with $(NH_4)_2S$ proves the absence of the last three of these elements. An orange-red filtrate proves the presence of molybdenum; a pure yellow one, its absence. A brown filtrate indicates the presence of vanadium.

2. $NH_4OH$ precipitates the hydrates of $SnO_2$, $TiO_2$, $Nb_2O_5$, $Ta_2O_5$, and $Fe_2O_3$ completely. If present alone, $H_2WO_4$ passes completely into solution in $NH_4OH$, and both it and $H_2MoO_4$ remain in solution upon adding $(NH_4)_2S$. The $SnO_4H_4$ dissolves completely upon digesting with $(NH_4)_2S$; so do any quantities of tungsten, molybdenum, or vanadium that may be present with it. When the elements that give rise to an $(NH_4)_2S$ precipitate are present, tungsten and molybdenum may be carried down with them in considerable quantity, and the latter element imparts to the precipitate an orange or red color, which is only very slowly removed by washing, but rapidly by digestion with $NH_4OH$. $(NH_4)_2S$ converts $FeO_3H_3$ to black FeS, the presence of which often gives rise to a dark-colored precipitate. Molybdenum, even in quantity of 1 mgm., imparts an orange-red color to the $(NH_4)_2S$ solution; vanadium gives a yellowish-brown color.

**Procedure 36.** — Transfer the precipitate insoluble in $NH_4OH$ and $(NH_4)_2S$ (P. 35), with the filter if necessary, to a casserole. Pour over it a mixture of 5–15 ccm. 3% $H_2O_2$ and 1–3 ccm. HCl (1.12); heat till the $H_2O_2$ begins to decompose rapidly, stir for 2–3 minutes, and filter through a washed filter, using suction if the residue is large. [If the residue is large and the solution strongly colored, dissolve the residue in HF, and treat the solution of it again by P. 33, 35, and 36,

omitting only the addition of $(NH_4)_2S$.] Wash the residue. (Residue, P. 37; solution, P. 38.)

*Notes.* — 1. A yellow or orange-red coloration of the $H_2O_2$ solution proves the presence of titanium; a colorless solution proves its absence. A residue undissolved by $H_2O_2$ is not a proof of the presence of tantalum.

2. When a large quantity of titanium is present, a considerable proportion of it may remain undissolved by the $H_2O_2$ and HCl, and this cannot usually be dissolved by treatment with a fresh portion of the mixture. Since the presence of much titanium interferes with the subsequent tantalum test, it must be removed by solution in HF, evaporation with $H_2SO_4$, precipitation with $NH_4OH$, and retreatment with $H_2O_2$, as directed. Moderate quantities of niobium dissolve completely, or almost completely, in the mixture of $H_2O_2$ and HCl. Tantalum, whether present in small or large quantity, divides itself between the residue and solution so that each contains, roughly, one-half of it. When tin and titanium are both present in the substance in considerable quantity, the former element is retained in large quantity in the $(NH_4)_2S$ precipitate, and a residue insoluble not only in $H_2O_2$, but also in strong HF, is obtained. It may be brought into solution, if desired, by fusion with $Na_2CO_3$ and S.

3. The HCl is added to the $H_2O_2$ to promote the solution of the $H_2TiO_3$, and to intensify the color produced by it.

4. If titanium is present in quantity even as small as 0.1 mgm., the $H_2O_2$ solution will have a distinct yellow color. If present in quantity as large as 100 mgm., the solution will have a deep orange-red color. The production of this yellow or orange-red color constitutes the test for titanium. When it is present alone in quantity as large as 2 mgm., and niobium is absent in considerable proportion, a confirmation is furnished later by the reddish violet color produced when zinc is added. To determine the approximate quantity present, the color may be compared with that given by dissolving a weighed portion of pure $TiO_2$ in a little HF, evaporating with 1 ccm. $H_2SO_4$ (1.84) to the fuming point, adding 10 ccm. $H_2O_2$, and diluting measured portions of this solution till the same color is obtained as that of the solution to be tested.

5. Vanadium in fairly small quantity also gives an orange-yellow or orange-red color to $H_2O_2$ solution; but this element rarely remains with those of the tungsten group, and the small quantity that may be present with them passes into the $(NH_4)_2S$ solution. Molybdenum gives a pure yellow color, but it is very much fainter at the same concentration. Tungsten gives no color.

6. The yellow or red color of the titanium solution is probably due to the formation of a double compound $TiO_2.xH_2O_2$.

**Procedure 37.** — Support the filter containing the precipitate insoluble in $H_2O_2$ and HCl (P. 36) upon a platinum ring, and pour through it repeatedly a portion of about 2 ccm. 48% HF. Add to the solution 1 ccm. $HNO_3$ (1.42), and evaporate it just to dryness. Dissolve the residue in 1 ccm. HF, add 0.5 gm. solid $K_2CO_3$, evaporate the solution to dryness, and heat the residue until, and only until, it becomes enamel white. Dissolve it in 2–3 ccm. of water, boil the solution down to about 0.5 ccm., add 0.5 ccm. water, and allow the solution to stand for 10 minutes. If a coarsely crystalline substance separates, warm the liquid slightly, add water little by little until it is dissolved, and allow the solution again to stand for 10 minutes. [If a coarsely crystalline substance separates in such large quantity that more than 2 ccm. water are required for its solution, add 1 ccm. $H_2SO_4$ (1.84), evaporate the mixture to the fuming point, add it to 5 ccm. water, and treat the solution by P. 35, 36, and 37.] (Precipitate and solution, reject.)

*Notes.* — 1. A heavy white or grayish, translucent, viscous-seeming precipitate, but not a coarsely crystalline or light flocculent one, proves the presence of tantalum; the non-formation of such a precipitate, its absence.

2. The HF solution is evaporated before adding the $K_2CO_3$, to volatilize any $SiO_2$ that may have been taken up from the dishes and filter paper used, for this may cause the tantalum to remain in solution. The $HNO_3$ is added to prevent any loss of tantalum by volatilization (see P. 3, N. 4).

3. When much tantalum is present, a loose, white, crystalline precipitate of $K_2TaF_7$ forms when the $K_2CO_3$ is added; for 10 ccm. of the saturated solution of this salt in water to which a very small quantity of HF is added contains only 23 mgm. Ta. But, when it is present in small quantity, it is necessary to remove the excess of HF by evaporation and ignition, and to boil the solution of the residue as directed, in order to convert this fluoride into the far less soluble oxyfluoride ($2K_2TaF_7.Ta_2O_5$). This oxyfluoride separates as a heavy, white, translucent, viscous-seeming powder of very characteristic appearance. If the residue is too strongly heated, the tantalum separates in a lighter, more flocculent, less characteristic form.

4. $K_2TiF_6$ is, like $K_2TaF_7$, a difficultly soluble substance, 10 ccm. of its saturated solution in water at 20° containing 25 mgm. Ti; and this may separate at the end of the tantalum test, in case the $H_2O_2$ failed to dissolve out all the titanium. It is readily distinguished, however, by its appearance in the form of white, semi-transparent, granular crys-

tals, and it is redissolved by gentle warming and slight dilution of the solution, which have little effect on the tantalum compound after it has once separated.

5. $K_2NbOF_5$ is far more soluble than the double fluorides of titanium and tantalum; thus 10 ccm. of a saturated solution of $K_2NbOF_5$ at 20° contains 250 mgm. Nb. When precipitated, it resembles $K_2TiF_6$ in appearance. The presence of a moderate quantity of niobium does not, therefore, by its separation, interfere with the tantalum test; for even if a precipitate is produced in the very concentrated solution, it dissolves on the addition of a little water. Moreover, the presence of niobium does not prevent the separation of the $2K_2TaF_7.Ta_2O_5$.

**Procedure 38.** — Add 1–2 ccm. $H_2SO_4$ (1.84) to the $H_2O_2$ solution (P. 36) of the $(NH_4)_2S$ precipitate, and evaporate until the $H_2SO_4$ begins to fume strongly. Cool completely, pour the solution into 1 ccm. HCl (1.12), add a little granulated Zn, and let the action continue for two or three minutes, noting any color effect. Dilute the solution with 4 ccm. water and divide it into two parts. Pour one-third of it through a column of finely granulated Zn 5 cm. in height, contained in a small, straight drying tube (1–1.5 cm. in diameter) whose bulb is stuffed tightly with glass-wool, and through which previously 5–10 ccm. HCl (1.02) have been poured, to make sure that the runnings are perfectly clear. Wash out the tube with 3–5 ccm. HCl (1.02). Allow the solution and washings to run directly into 5 ccm. of nearly saturated $HgCl_2$ solution to which 0.5 ccm. HCl (1.12) has been added. Note whether a precipitate forms immediately.

If no precipitate results, pour also the remaining two-thirds of the $H_2SO_4$ solution through the zinc column to confirm this fact. (Solution, reject.)

If a precipitate results, proceed with the remaining two-thirds of the $H_2SO_4$ solution as follows: Make alkaline with $NH_4OH$, add a sufficient excess to dissolve the precipitated $ZnO_2H_2$ and filter. (Filtrate, reject.) Transfer the precipitate, with the filter if necessary, to a platinum crucible, heat until the mass becomes dry and the filter is incinerated, mix the residue in a mortar with six times its volume of a mixture of equal weights of $Na_2CO_3$ and S, and heat the mixture in a covered porcelain crucible to a dull red heat for 15 minutes. Cool, and treat the fused mass in the crucible with successive portions of hot water till it is disintegrated. Filter through a washed filter and wash the residue. (Filtrate, P. 39, uniting it with the filtrate of P. 35.)

Transfer the precipitate, with the filter if necessary, to a platinum dish, and treat it with 5 ccm. 48% HF till it is dissolved, continuing the treatment for some hours if necessary. Add 1–2 ccm. $H_2SO_4$ (1.84) and evaporate until the $H_2SO_4$ begins to fume strongly. [If the liquid is dark colored, add $HNO_3$ (1.42) and evaporate again.] Cool, dilute with 5 ccm. HCl (1.02), and pour the mixture through a zinc column prepared as before, collecting the effluent in $HgCl_2$ solution. (Precipitate and solution, reject.)

*Notes.* — 1. A reddish violet color appearing at once on the addition of Zn confirms the presence of titanium; a blue color indicates that of niobium or tungsten. If there is no immediate precipitate in the $HgCl_2$ solution, this proves the absence of niobium; an immediate precipitate obtained in the first test shows the presence of niobium, tungsten, or molybdenum; if again obtained after the fusion with $Na_2CO_3$ and S, and if more than a mere turbidity, it proves the presence of niobium.

2. The solution is evaporated with $H_2SO_4$ to remove the $H_2O_2$. It is then diluted with only a little HCl and treated with a little Zn, so as to make the color indications for titanium and niobium as delicate as possible.

3. If titanium is present alone in quantity as large as 2 mgm., a distinct reddish violet color is produced; if in quantity as large as 20 mgm., a dark, reddish violet color results. If, however, a titanium solution containing HF — even the small quantity of it that remains after the evaporation of such a solution to slight fuming with $H_2SO_4$ — is treated with Zn, a green coloration is produced. If niobium is present alone in quantity as large as 0.5 mgm., a pale blue color results; if in quantity as large as 20 mgm., a very dark blue color is produced. When the reduction becomes complete, as is the case after the solution has been poured through the zinc column, a dark brown color is obtained, even with a fairly small quantity of niobium. If titanium is present in predominating quantity, the niobium indication is obscured. Neither tantalum nor zirconium produces any coloration.

4. The salts both of titanium dioxide and niobium pentoxide are reduced to a lower state of oxidation ($Ti_2O_3$ and $Nb_2O_3$, respectively) by the nascent hydrogen; but the lower oxide of niobium alone has sufficient reducing power to convert $HgCl_2$ into HgCl. The test is delicate, but not very characteristic. Neither tantalum, zirconium, titanium, iron, nor tin produces the same result under the conditions of the experiment; but titanium in large quantity may do so if the $HgCl_2$ solution is allowed to stand, even for 15 minutes. Tantalum or zirconium is not reduced at all by Zn, and tin is reduced to the metallic

state. Iron is converted into a ferrous salt, but this does not reduce $HgCl_2$. The lower oxides of tungsten, molybdenum, and vanadium ($WO_2$, $Mo_2O_3$, and $V_2O_2$) produced by the action of Zn do, however, cause reduction of $HgCl_2$; moreover, these elements are retained in considerable quantity in the $(NH_4)_2S$ precipitate, when much titanium is present. If a precipitate forms in the $HgCl_2$ solution, it may therefore arise from one of these elements and not from niobium; and it is then necessary to remove them from the remaining two-thirds of the $H_2SO_4$ solution by fusion with $Na_2CO_3$ and S, and again apply the reduction test. Repeated digestion of the $(NH_4)_2S$ precipitate with $NH_4OH$ and $(NH_4)_2S$ is much less effective. Even after the fusion with $Na_2CO_3$ and S, traces of tungsten may remain in the titanium residue if much tungsten was present in the solution treated with $(NH_4)_2S$; and a slight turbidity (not more than that given by 1 mgm. Nb) may result therefrom in the second test with Zn and $HgCl_2$. In such a case, a very slight turbidity must not, therefore, be regarded as proof of the presence of niobium, but a considerable one is conclusive evidence of it. A quantity of niobium as small as 2 mgm. may be lost in the processes connected with the fusion, but not a larger quantity.

5. The fusion with $Na_2CO_3$ and S is also necessary, in order to make possible the detection of small quantities of tungsten, which are carried down almost completely with the titanium hydroxide when much of this is present. It is on this account, also, that the aqueous solution of the fused mass is united with the original $(NH_4)_2S$ filtrate.

**Procedure 39.** — Combine the filtrate from the $(NH_4)_2S$ precipitate (P. 35) with that from the $Na_2CO_3$ and S fusion (P. 38). Make the solution distinctly acid with $H_2SO_4$ (1.20), shake, and filter, using suction if the precipitate is large. (Precipitate, if its color is that of precipitated sulphur, reject; if not, P. 41. Filtrate, if a sulphide has been precipitated from it or if it is at all yellow, or if it contains phosphate, P. 40; otherwise, reject.)

*Note.* — 1. Molybdenum, tin, and tungsten, when present in the $H_2SO_4$ precipitate, even in quantity as small as can be detected by the subsequent tests for these elements, impart either a dark color or a deep yellow color to that precipitate. Therefore, if the precipitate has the color of pure sulphur, it is not necessary to examine it further. In a doubtful case, the precipitate should be ignited as described in P. 41 and the amount of the residue estimated or weighed. Molybdenum is completely or nearly completely precipitated by the $H_2SO_4$, and tin is completely precipitated by it. Tungsten, when present in

large quantity, divides itself between the precipitate and filtrate; when present alone in small quantity it passes almost wholly into the filtrate, to which even a quantity of 1 mgm. imparts a distinct yellow color. In the presence of the other elements precipitated as sulphides, a small quantity of tungsten may, according to the conditions, either be completely precipitated with them, or it may pass entirely into the filtrate, and without imparting to it a yellow color. If a precipitate of sulphide is obtained, it is therefore necessary to test the filtrate for tungsten by P. 40, even though it be colorless. In the presence of phosphate, too, even a considerable quantity of tungsten seems to pass completely into the filtrate.

**Procedure 40.** — If the filtrate from the $H_2SO_4$ precipitate (P. 39) requires examination (see P. 39), evaporate it till the residue becomes almost dry, transfer the latter to a platinum crucible, and ignite as long as $H_2SO_4$ fumes are expelled. Add to the residue a little HF and a few drops $H_2SO_4$, and again evaporate till fuming ceases. Add to the residue twice its volume of solid $Na_2CO_3$, and heat for 5 minutes over a powerful burner. Cool, fill the crucible with water, heat till the mass is dissolved, and filter if the solution is not clear. Acidify the solution strongly with $HNO_3$, and boil. If no precipitate separates, evaporate the liquid to dryness, moisten with $HNO_3$ (1.20), again evaporate to dryness, warm the residue with enough $HNO_3$ (1.10) to dissolve the salt present, and allow time for any precipitate to settle out. Whether a precipitate forms or not, add 2 ccm. $H_2SO_4$ (1.84), evaporate to the fuming point, dilute with 5 ccm. HCl (1.02), and add a little granulated Zn. (Residue and solution, reject.)

*Notes.* — 1. The treatment with HF and $H_2SO_4$ serves to remove any $SiO_2$ that may have been introduced by the action of the alkaline solutions on the vessels or in the fusion with $Na_2CO_3$ and S. If not removed, it would separate with the $H_2WO_4$ when the aqueous solution of the fused mass is evaporated with $HNO_3$, and might obscure the test for tungsten.

2. When $HNO_3$ is added to an alkaline tungstate, $H_2WO_4$ separates as a white, flocculent precipitate, which upon boiling turns yellow and becomes more compact. A very small quantity of tungsten, however, may not precipitate in this way; but it is separated as a heavy yellow powder, or as yellow flocks, or as a yellow stain on the sides of the dish, when the solution is repeatedly evaporated with acid.

3. In case a distinct yellow precipitate separates from the $HNO_3$ solution, the evaporation with $H_2SO_4$ and the addition of Zn, whereby

a deep blue coloration and precipitate are produced if tungsten is present, serves only as an (almost superfluous) confirmation of the presence of that element. If, however, phosphate is present, and there is no yellow precipitate, the reduction test with Zn is essential, since $H_2WO_4$ does not separate from a solution containing a corresponding amount of this acid radical. Even a large quantity of phosphate does not, however, prevent the production of a strong blue color with one milligram of tungsten.

**Procedure 41.** — If it is large enough in quantity, separate the $H_2SO_4$ precipitate (P. 39) from the filter, and transfer it to a porcelain crucible. If small in quantity, pour a portion of 2–3 ccm. $(NH_4)_2S$ repeatedly through the filter till the precipitate is dissolved, collect the solution in a porcelain crucible, and evaporate it to dryness. Provide the crucible with a perforated porcelain cover through which passes a porcelain tube. Pass through the tube into the crucible a slow current of $H_2S$ gas, and heat the crucible (preferably within a cylindrical jacket with open ends, if the precipitate is large) first gently, then more strongly, and finally, for 5–30 minutes, or until the whole mass becomes black, to the highest temperature attainable with a powerful burner. Allow the crucible to cool with the $H_2S$ gas still passing through it. Rub its contents to a powder, and transfer them to a small Erlenmeyer flask. Pour into the crucible, if some of the substance is adhering to it, 2–3 ccm. HCl (1.20), warm, and pour the solution, together with 5–10 ccm. more HCl (1.20), into the flask. Cover the flask and boil the liquid gently as long as the vapors continue to blacken filter-paper wet with a NaOH solution of $Pb(C_2H_3O_2)_2$, replacing the acid which evaporates. Dilute the solution with its own volume of water, filter, and wash the residue. (Residue, P. 43; solution, P. 42.)

*Note.* — 1. Precipitated $WS_3$ and $V_2S_5$ are sufficiently soluble in hot strong HCl to make their separation from $SnS_2$ and $Sb_2S_5$ by this solvent impracticable. By ignition in an atmosphere of $H_2S$, however, they are converted into $WS_2$ and $VS_2$, which are entirely insoluble in boiling HCl (1.20). The ignition also serves to volatilize any $As_2S_5$ present, which otherwise would prevent the precipitation of $H_2WO_4$ in the subsequent test for tungsten. By the ignition $SnS_2$ and $Sb_2S_5$ are converted into black SnS and $Sb_2S_3$ respectively, which dissolve readily in HCl (1.20). If the ignition is not prolonged or intense enough, the hydrated $SnS_2$ is converted only into "mosaic gold" ($SnS_2$), consist-

ing of golden yellow scales with metallic lustre; and this is only very slowly dissolved by the hot acid. The ignition must therefore be continued till the entire mass becomes black. Both $MoS_3$ and the $MoS_2$ into which it is converted by ignition are entirely unattacked by boiling hydrochloric acid. The $H_2S$ prevents the conversion of the sulphides into oxides, which occurs if air has access to them at a high temperature.

**Procedure 42.** — Evaporate the HCl solution (P. 28) to a volume of 2–3 ccm., and add an equal volume of water and about 0.5 gm. finely granulated Zn. Allow the action to continue for 10 minutes. Decant the solution completely from the residue, allow any suspended particles to settle out from the liquid, and decant again. (Solution, reject.) Add to the united residues 2–4 ccm. HCl (1.20), heat gently till the Zn has all dissolved, and then just to boiling unless the residue has previously disappeared, add half a volume of water, and pour the solution through a small filter into 5 ccm. nearly saturated $HgCl_2$ solution. (Residue, precipitate, and solution, reject.)

*Notes.* — 1. If tin seems to be present in considerable quantity (10 mgm. or more), it may advantageously be tested for more simply by adding a portion of the HCl solution of the ignited sulphide, immediately after the $H_2S$ is completely boiled out, to $HgCl_2$ solution; and in case a precipitate results, the treatment with Zn may be dispensed with; for after the ignition the tin is in the stannous state, and no other element can be present which reduces $HgCl_2$, since ignited $WS_2$, $MoS_2$, and $VS_2$ are entirely insoluble in HCl, and since $SbCl_3$ does not cause reduction. In case, however, only a small quantity of tin (5 mgm. or less) is present, it may become completely oxidized during the boiling of the HCl solution. In order that the tin test may be delicate, it is therefore necessary to follow the procedure and observe the precautions above indicated — especially to allow time for the complete reduction of the tin salt by the Zn, to secure solution of the tin by heating sufficiently with strong HCl, and to prevent oxidation of the stannous salt by carrying out rapidly the last steps in the process. By observing these precautions one milligram of tin is readily detected.

2. It is not necessary to test for antimony at this point, since it would have been precipitated in large part by $H_2S$ in the first procedure of this group, and would pass, partly through that precipitation and partly directly, into the main $HNO_3$ solution.

**Procedure 43.** — Heat the residue insoluble in HCl (P. 41) in a covered vessel on a steam bath with 2–8 ccm. $HNO_3$ (1.42) and 1–2

ccm. HCl (1.20) until it all dissolves, with the exception of a few black particles, or becomes pure yellow. If there is a residue, add an equal volume of water, allow the residue to settle, and decant the liquid through a filter. To the filtrate, or to the unfiltered solution if there was no residue, add 2–3 ccm. $H_2SO_4$ (1.84), evaporate till this acid fumes slightly, keep at that temperature for 3–5 minutes, cool, add 5 ccm. water, allow the residue to settle, and decant the solution through a filter. (Residues, P. 44; solution, P. 45.)

*Notes.* — 1. Even 100 mgm. of ignited $MoS_2$ are completely dissolved by 10 ccm. of the mixture of $HNO_3$ and HCl; and as a larger quantity cannot be present in this precipitate, there is no danger of its interfering with the tungsten test, provided the acid used is not evaporated off. If, however, the acid solution is allowed to concentrate, $MoO_3$ may separate as a white or light yellow powder, which will redissolve only in a very large quantity of $HNO_3$. If this seems to have occurred, the residue should not be separated from the solution till after the evaporation with the $H_2SO_4$. Black particles of carbon are usually left undissolved by the $HNO_3$ and HCl.

2. Even a small quantity (1–2 mgm.) of tungsten, when present alone at this point, is readily detected by its separation as a yellow residue from the $HNO_3$ and HCl solution; but when much molybdenum (100 mgm.) is also present, a considerable quantity of tungsten (at least 4 mgm.) remains in solution. After the heating with the $H_2SO_4$, however, a quantity even as small as 2 mgm. always separates as a yellow, compact powder.

3. If no yellow residue is obtained here or from the filtrate from the $H_2SO_4$ precipitate (P. 40), it does not show the absence of tungsten in the substance, since it may have passed entirely into the main $HNO_3$ solution (P. 6), as mentioned in P. 5, N. 1.

**Procedure 44.** — Add to the residues insoluble in $HNO_3$ and $H_2SO_4$ (P. 43) 2–3 ccm. HCl (1.12), evaporate to dryness, add 2 ccm. HCl (1.12) and a few granules of Zn.

*Note.* — 1. The evaporation with HCl removes the $HNO_3$ adhering to the residue. Even in the presence of 0.5 mgm. W, a distinct blue coloration results, while with a somewhat larger quantity the mixture assumes a dark blue color of great intensity. This color is due to a suspended precipitate, which soon coagulates, consisting of a hydrated oxide intermediate between $WO_3$ and $WO_2$. Molybdenum when present in strong HCl solution, such as is directed to be used in this test,

does not give a blue color with Zn, but there results a series of colors, — yellow, dark orange, dark green, and, finally, dark olive brown. In dilute HCl solution, however, molybdenum, even in moderate quantity, gives rise at once to a deep blue coloration of the solution.

**Procedure 45.** — Add to the $H_2SO_4$ solution (P. 43) of the ignited sulphides 1–2 ccm. 10% KSCN solution and some granulated Zn.

*Note.* — 1. A red coloration which appears on the addition of the Zn shows the presence of molybdenum. Iron, if present as impurity, will give a red color with the KSCN alone, but this disappears almost immediately on the addition of the Zn. A negative result is of no significance, since molybdenum may have passed entirely into the main $HNO_3$ solution.

## Test Analyses.

At different stages in the development of the process above described, numerous analyses were made to test its efficiency. Nearly all of those which were made after integral parts of the procedure assumed final form are reproduced in the tables below. In these tables the numbers in each vertical column show the weights in milligrams of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S — that is, when the element was present, that the test for it, however small, was unmistakable and therefore conclusive; and when the element was absent, that a good blank test was obtained. When the test was very small in comparison to the quantity of the element present, though still unmistakable, or when in its absence (especially in the niobium and tantalum tests) there was obtained not a perfect blank, but yet one good enough to warrant the conclusion that less than one milligram is present, this is sometimes indicated by the symbol S−. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing, for example, to the test being obscured by some other element, this is indicated by the letter D. When the test was not tried, if the element was present, a dash is used in place of a letter, or, if the element was not present, the whole space is left blank.

The first series of twenty-three analyses were made by Mr. D. P. Smith at a time when the procedure through the analysis of the titanium, tantalum, and niobium hydroxide precipitate was in nearly its final form, but when the tin and tungsten were still being separated by heating the moist, precipitated sulphides with strong hydrochloric acid. Therefore, owing to the solubility of tungsten sulphide under these conditions (see G. D., § 10), the failures to detect tungsten in the presence of much tin in these analyses do not show a defect in the final procedure. In all of the analyses of this series, before testing for tungsten, the sodium carbonate solution (P. 40) obtained from the filtrate from the sulphuric acid precipitate was united with an ammonia solution of the residue left upon treating the sulphides with nitric acid (P. 43), and the mixed solutions were then evaporated with nitric acid to separate the yellow tungstic acid. The results given for the niobium tests are always those obtained in the second test with mercuric chloride after the fusion with sodium carbonate and sulphur, when a precipitate obtained in the first test made this fusion necessary.

A second series of analyses (Nos. 24–29) were made by Mr. F. M. Eaton, who had had no previous experience in connection with this process and who was given no information in regard to it other than that contained in a copy of the "Procedure and Notes." The procedure was then in final form, except that the hydrochloric acid solution of the ignited sulphides was tested for tin by adding it directly to mercuric chloride, instead of first reducing it with zinc, which accounts for the repeated failures to detect small quantities of tin (see P. 42, N. 1). The results with niobium were those obtained in the second mercuric chloride test after the fusion with sodium carbonate and sulphur, except where otherwise indicated by footnotes. The sulphuric acid precipitate and the filtrate from it were separately tested for tungsten.

The third series of analyses (Nos. 30–39) were made according to the final procedure in every respect, in part by Mr. D. P. Smith and in part by Mr. F. M. Eaton, as indicated by the initials at the head of the columns. As a matter of information, the results of both the first and second mercuric chloride tests for niobium are recorded, but it is only the second one that is really significant of the presence or absence of that element, except when the first test gives a negative result. The results of testing for tungsten both the sulphuric acid precipitate

(by P. 41 and 43) and the filtrate from it (by P. 40) are also shown, but the detection of it in either place is, of course, a satisfactory result. In those analyses to the numbers of which a star is attached the contents of the mixture were unknown to the analyst in advance. Such unknown mixtures were not analyzed in greater number, because to a person having any experience with the process the interpretation of the tests is scarcely ever doubtful; and as long as the procedure is in process of development, it is advantageous that the analyst know immediately of failures to secure the right result.

The fourth series of analyses (Nos. 40–46) were also made after the procedure was fully developed, but they have reference only to the detection of tin, tungsten, molybdenum, and phosphate in the presence of one another.

FIRST SERIES.

| T. A. No. | 1[1] | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Analysis begun at | P. 3 | P. 3 | P. 3 | P. 33 | P. 33 | P. 33 | P. 33 | P. 33 |
| Ta . . . . . | 0 S | 0 S | 2 F | 2 S | 2 S | . . . | . . . | 2 S |
| Ti . . . . . | 500 S | 100 S | 300 S | 300 S | 300 S | 300 S | 300 S | 300 S |
| Nb . . . . . | 0 S | 0 S | 1 F | . . . | . . . | 0 S— | 0 S | 0 S— |
| Sn . . . . . | 1 F | 1 S | 300 S | 3 S | 300 S | . . . | . . . | 2 S |
| W . . . . . | 1 F | 2 S | 1 F | 300 S | 5 F | 300 S | 5 S | 300 S |

| T. A. No. | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|
| Analysis begun at | P. 33 | P. 33 | P. 33 | P. 33 | P. 33 | P. 33 | P. 33 | P. 5 |
| Ta . . . . . | 0 D[2] | 2 S | 0 S—[2] | . . . | 2 S | 100 S | 2 S | 2 S |
| Ti . . . . . | 300 S | 3 S | 300 S | 200 S | 300 S | 2 S | . . . | 2 S |
| Nb . . . . . | 2 F | 0 S | 5 S | 2 S[3] | . . . | 2 S[3] | 100 S | 0 F[4] |
| Sn . . . . . | 300 S | 300 S | 300 S | . . . | . . . | . . . | . . . | . . . |
| W . . . . . | 2 F | 300 S | 5 F | . . . | . . . | . . . | . . . | 3 F[5] |
| Mo . . . . . | . . . | . . . | . . . | . . . | . . . | . . . | . . . | 500 S |

FIRST SERIES — *Continued.*

| T. A. No. | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
|---|---|---|---|---|---|---|---|
| Analysis begun at | P. 31 | P. 33 | P. 33 | P. 33 | P. 33 | P. 33 | P. 33 |
| Ta . . . . . | . . . | . . . | . . . | . . . | . . . | . . . | . . . |
| Ti . . . . . | 300 S | 5 S | . . . | 5 S | 300 S | 300 S | 300 S |
| Nb . . . . . | 0 S | . . . | 5 S | . . . | . . . | . . . | . . . |
| Sn . . . . . | . . . | 300 S | 300 S | . . . | . . . | . . . | . . . |
| W . . . . . | . . . | . . . | . . . | 300 S | 5 F | 5 S | 10 S |
| Mo . . . . . | 300 S | . . . | . . . | . . . | . . . | . . . | . . . |

SECOND SERIES.

| T. A. No. | 24 | 25 | 26 | 27 | 28 | 29 |
|---|---|---|---|---|---|---|
| Analysis begun at | P. 31 | P. 31 | P. 31 | P. 31 | P. 31 | P. 33 |
| Sb . . . . . | 3 S | 2 S | 1 S | 3 S | . . . | . . . |
| Ta . . . . . | 3 S | 2 S | 1 S | 3 S | 0 S | 2 S |
| Ti . . . . . | 3 S | 1 S | 1 S | 3 S | 2 S | 300 S |
| Nb . . . . . | 3 S | 2 F | 1 S—[8] | 3 S | 2 F[9] | 0 S[7] |
| Sn . . . . . | 3 F | 2 F | 1 F | 3 S | 2 F | 2 F |
| W . . . . . | 3 F | 300 S | 1 F | 3 S[6] | 2 F | 2 F |
| Mo . . . . . | . . . | . . . | . . . | . . . | 300 S | . . . |

THIRD SERIES.

| T. A. No. | 30* | 31* | 32* | 33* | 34 |
|---|---|---|---|---|---|
| Analyst. | D. P. S. | F. M. E. | F. M. E. | F. M. E. | D. P. S. |
| Analysis begun at | P. 31 | P. 31 | P. 33 | P. 31 | P. 31 |
| Sb | 0 S | 400 S | . . . | 0 S | . . . |
| As | 2 S | . . . | . . . | 2 — | . . . |
| Ta | 0 F | 0 D[10] | 2 S—[11] | 2 S | 0 S |
| Ti | 2 S | 2 S | 400 S | 400 S | 2 S |
| Nb, First test | S | S | F | F | S |
| Nb, . . . . . | 2 | 2 | 0 | 0 | 0 |
| Nb, Second test | — | S | S | S | — |
| Sn | 400 S | 2 F | 2 F | 4 F | 2 F |
| W, P. 40 | F | F | S | S— | S |
| W, . . . . . | 2 | 2 | 4 | 400 | 4 |
| W, P. 43 | — | F | S— | S | F |
| Mo | . . . | 0 S | 2 S | 2 S | 400 S |

| T. A. No. | 35 | 36 | 37* | 38 | 39 |
|---|---|---|---|---|---|
| Analyst. | D. P. S. | D. P. S. | F. M. E. | D. P. S. | D. P. S. |
| Analysis begun at | P. 31 | P. 31 | P. 31 | P. 31 | P. 35 |
| Sb | . . . | 400 S | . . . | . . . | . . . |
| As | . . . | . . . | . . . | 100 S | . . . |
| Ta | 0 D[2] | 2 S | 2 S | 0 S | . . . |
| Ti | 400 S | 2 S | 2 S | 2 S | 400 S |
| Nb, First test | F | S | S | S | F |
| Nb, . . . . . | 0 | 2 | 2 | 0 | 0 |
| Nb, Second test | F[4] | F | F | — | S |
| Sn | 4 F | 4 S | 4 F | 400 S | . . . |
| W, P. 40 | F | S | F | F[12] | . . . |
| W, . . . . . | 4 | 4 | 4 | 4 | . . . |
| W, P. 43 | F | F | S— | F | . . . |
| Mo | 400 S | 2 S | 400 S | . . . | 200 S |

FOURTH SERIES.

| T. A. No. | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 |
|---|---|---|---|---|---|---|---|---|
| Analyst. | D. P. S. | D. P. S. | D. P. S. | F. M. E. | F. M. E. | F. M. E. | F. M. E. | D. P. S. |
| Analysis begun at | P. 33 | P. 33 | P. 33 | P. 35 | P. 31 | P. 35 | P. 35 | P. 35 |
| Sn . . . . . | 300 S | 300 S | 1 S | 30 S | 8 S | . . . | . . . | . . . |
| W P. 40 . . . | — | — | — | S[13] | — | — | F | — |
| W . . . . . | 3 | 1 | 300 | 8 | 8 | 4 | 2 | 2 |
| W P. 43 . . . | S | S | S | F | S | S | S— | F |
| Mo . . . . . | . . . | . . . | . . . | . . . | 400 S | 100 S | 100 S | 100 S |
| $PO_4$ . . . . . | . . . | . . . | . . . | 20 S | . . . | . . . | . . . | . . . |

[1] This mixture also contained 1 mgm. Sb and 1 mgm. Mo, and these were detected in the $H_2S$ precipitate.

[2] A small precipitate (very slight in T. A. 11) was obtained, owing to a little tantalum in the titanium used. To show the presence of this impurity, 400 mgm. Ti were alone put through P. 33, 35, and 36; a precipitate corresponding to that given by 2 mgm. Ta was obtained.

[3] This was the result even after the fusion with $Na_2CO_3$ and S, which was made to see whether it would result in loss of the niobium.

[4] In this analysis the $(NH_4)_2S$ precipitate was not redigested with $NH_4OH$, as directed in P. 35, when much molybdenum is present.

[5] $H_2SO_4$ was not used, as directed in P. 43, to cause the tungsten to separate.

[6] Tungsten was detected only in the filtrate.

[7] Fusion with $Na_2CO_3$ and S was omitted, since no precipitate formed in first $HgCl_2$ test.

[8] Fusion with $Na_2CO_3$ and S was omitted, since the precipitate in first $HgCl_2$ test was too slight.

[9] There was a very slight turbidity in the first $HgCl_2$ test.

[10] A light, flocculent precipitate separated on standing.

[11] A light, flocculent precipitate first separated; but upon repeating the treatment of P. 36, it assumed the characteristic appearance of the tantalum precipitate.

[12] The reduction test with Zn at end of P. 40 was not tried, which may have been necessary, since the arsenic, if present in this solution, would have prevented the separation of tungstic acid.

[13] No yellow $H_2WO_4$ separated, but a decided blue coloration was obtained with Zn.

In order to summarize the results of these analyses, and form thereby a judgment in regard to the efficiency of the procedure, each element will be considered separately.

*Tantalum.* — This element was present in quantity of 2 mgm. in fourteen of the mixtures analyzed, of 3 mgm. in two of them, and of 1 mgm. in one of them. A satisfactory test for it was obtained in every case, except one (T. A. 3) in which 300 mgm. of titanium and 300 mgm. of tin were simultaneously present, and it was found, even in this mixture, in a second analysis (T. A. 5). Its detection succeeded repeatedly in the presence of 300 mgm. of titanium, or in that of 300 mgm. tungsten, or in that of 300 mgm. tin. It succeeded also in the cases where 400–500 mgm. molybdenum (T. A. 16, 37), or 100 mgm. niobium (T. A. 15), or 400 mgm. antimony (T. A. 36) were present. Two milligrams can therefore always be detected.

The "blank" tests for tantalum (that is, those in the absence of this element) were somewhat inconclusive in those mixtures containing much titanium (T. A. 9, 11, 32, 35), owing to the presence of a minute quantity of tantalum in the titanium sample used; but the precipitates were always very small (1–2 mgm.), and there is little doubt that with pure material perfect blanks would be obtained. In two cases (T. A. 31, 32), also, a light, flocculent precipitate separated in place of the heavy, viscous one characteristic of tantalum. Good blanks were obtained in the other cases (T. A. 2, 28, 34, 38). While a further study of the blanks obtaining in testing for this element according to the procedure is desirable, especially since no good confirmatory test for it is known, yet it is hardly possible that error will be made, even with respect to small quantities, by any one who first makes himself familiar with the appearance of the potassium fluoxytantalate and fluotitanite.

*Niobium.* — There would be no difficulty whatever in detecting 2 mgm., or even less, of this element, provided the first test with mercuric chloride could be relied upon; but, owing to the possible presence of tungsten or molybdenum, it is ordinarily necessary to fuse with sodium carbonate and sulphur, and then apply a second test. The results show that under these circumstances 2 mgm. is near the limit of detection. This quantity was present in nine of the mixtures analyzed; and the second test failed in five, and succeeded in three of them (it being omitted in one case). Three milligrams were present in two mixtures and 5 mgm. in two others, and in all of these the test was satisfactory. It succeeded with 2 mgm. in the presence of 400 mgm. of antimony (T. A. 31), or of 200 mgm. of titanium (T. A. 12), or of 100 mgm. tantalum (T. A. 14), and with 5 mgm. in the presence of 300 mgm. of tin (T. A. 11, 19). — It seems safe to conclude that 3 mgm. can be detected under almost any conditions.

The question of blank tests for this element in the presence of much titanium, tungsten, or molybdenum is an especially important one, and many mixtures were prepared and analyzed with reference to it. A perfectly clear solution, or a slighter turbidity than would have resulted from 1 mgm. of niobium, was obtained in the second mercuric chloride test from nine mixtures containing 300–500 mgm. of titanium. In three of these mixtures 300–400 mgm. and in two of them 4–5 mgm. tungsten were simultaneously present. The result,

too, was satisfactory in the four cases where tungsten was present with only a small quantity of titanium. This was also true where the mixtures contained much tin, either with or without much tungsten. In two of the five mixtures (T. A. 16, 35) in which 300–500 mgm. of molybdenum were present, the second mercuric chloride test showed a decided turbidity, while in the other three (T. A. 17, 31, 39) a good blank was obtained; but in all these analyses except the last (T. A. 39) the ammonium sulphide precipitate was not redigested with ammonia — a precaution that was adopted only near the end of the work. — The results of the blank tests for niobium may therefore be considered satisfactory under all circumstances, provided regard is paid to all the precautions described in the procedure.

*Titanium.* — The results for this element require little discussion. The yellow or orange-red color produced with hydrogen peroxide constitutes so delicate a test that in every mixture containing 1 or 2 mgm. of it, it was conclusively detected. The test is so characteristic that blank tests were considered unnecessary, especially since its presence is ordinarily confirmed by the reddish-violet color produced with zinc.

*Tin.* — The only analyses in which the final procedure for the separation and detection of tin was employed are those of the third and fourth series; but Test Analyses 1, 2, and 8 also deserve consideration, since the omission of the ignition of the sulphide could hardly affect the tin test. The results show that 2 mgm. escape detection when 400 mgm. of either titanium (T. A. 32), antimony (T. A. 31), or molybdenum (T. A. 34) are present, and that this is true of even 4 mgm. in the presence of 400 mgm. of molybdenum (T. A. 37), or in the simultaneous presence of 400 mgm. of titanium and an equal quantity of molybdenum (T. A. 35) or tungsten (T. A. 33). On the other hand, the test succeeded with 4 mgm. of tin in presence of 400 mgm. of antimony (T. A. 36), with 8 mgm. of tin in the presence of 400 mgm. of molybdenum (T. A. 44), and with 1 mgm. of tin in the presence of 300 mgm. of tungsten (T. A. 42) or of 100 mgm. of titanium (T. A. 2). It seems therefore fair to set the limit of detection at 3 mgm. in the presence of much antimony or titanium, at 6 mgm. in that of much molybdenum, and at 1 mgm. in that of much tungsten.

Blank analyses were considered unnecessary, since experiments (see C. E., P. 41, N. 1) showed the complete insolubility in hot hydrochloric acid of the ignited sulphides of the other elements which reduce mercuric chloride.

*Tungsten.* — In the case of this element, all analyses except those of the first series were made by the final procedure. The analyses of the first series in which the test succeeded (T. A. 2, 7, 22, 23) also deserve consideration, since the omission in them of the ignition of the sulphide could only have the effect of making the test less delicate. It will be seen from the tables that the detection of 2 mgm. failed in the presence of 300–400 mgm. of antimony (T. A. 31) or of titanium (T. A. 29), or of 100 mgm. or more of molybdenum (T. A. 28, 31, 47); and that that of 4 mgm. failed in the simultaneous presence of 400 mgm. each of titanium and molybdenum (T. A. 35). On the other hand, 3 mgm. were detected when no other element was in great excess (T. A. 2, 27) or when much tin was present (T. A. 40, 41); and 4 mgm. were detected when the mixture also contained 400 mgm. of titanium (T. A. 32) or of antimony (T. A. 36), or 100 or more milligrams of molybdenum (T. A. 34, 37, 46). Eight milligrams were detected in the presence of 20 mgm. of phosphate (T. A. 43), but a less quantity could probably have been found. The limit of detection may therefore be set at 2 mgm. when it is present either alone or with a large quantity of tin, and at 3 or 4 mgm. when a large quantity of antimony, titanium, or molybdenum is simultaneously present.

Molybdenum and tin are the only elements that could give rise to a precipitate in a blank analysis at the point where the ignited sulphides are dissolved in nitric and hydrochloric acid (P. 43); and mistake from this source is entirely guarded against by the subsequent evaporation with sulphuric acid, and by the confirmatory test with zinc.

*Antimony, arsenic, and molybdenum.* — The final detection of these elements is effected in connection with the later groups. It is therefore sufficient to show that even a small quantity of any of them present in the solution of this group is precipitated by hydrogen sulphide from the hydrofluoric acid solution (P. 31). This is shown by the above analyses for 1 or 2 mgm. of antimony (T. A. 1, 25, 26) and of molybdenum (T. A. 1, 32, 33). Special experiments have confirmed this result, and have shown that 2 mgm. of arsenic are also precipitated (see C. E., P. 31, N. 3).

*Summary.* — The preceding discussion may be summarized by the following statements: Four milligrams of any element of this group, when present in the hydrofluoric acid solution at the start, can be detected with certainty by the procedure described in this article, even when a quantity as large as 300–400 mgm. of any other element of the

group is simultaneously present. Two milligrams of titanium, tantalum, antimony, arsenic, or molybdenum, or three of niobium can be detected with certainty in any combination whatever with other elements. Two milligrams of tin or tungsten can each be detected alone or in the presence of a very large quantity of the other, but not in the presence of a large quantity of the elements precipitated by hydrogen sulphide or ammonium sulphide. Eight milligrams of tungsten, and probably much less, can be detected in the presence of a considerable quantity of phosphate. There is no possibility of concluding that any absent element is present as a result of a failure of the final test to yield a blank, except in the cases of tantalum and niobium; and observance of all the precautions described and of the remarks as to the interpretation of the results will prevent any mistake in these cases.

In conclusion, it need hardly be said that skill in the manipulation of exact qualitative analysis and some slight experience with this process itself are essential in order to secure the degree of delicacy just referred to it. But the attempt has been made to make the directions so detailed and explicit that it is believed that an analyst possessing such skill will be able to approximate closely to these results after working through a single mixture containing small quantities of all the elements of the group.

## Confirmatory Experiments and References.

**G. D., § 4.** — See C. E., P. 35, N. 4, in regard to the separation of tungsten from titanium by digestion with $(NH_4)_2S$, and C. E., P. 38, N. 5, in regard to that by fusion with $Na_2CO_3$ and S.

For the separation of tungsten and titanium by fusion with $KNO_3$ and $K_2CO_3$, see Defacqz, *Compt. rend.*, **123**, p. 823 (1896).

A mixture of 10 mgm. W and 300 mgm. Ti in HF solution was treated by P. 33, 35, 36, and 38, except that the fusion with $Na_2CO_3$ and S was replaced by the following process: the $NH_4OH$ precipitate obtained after the treatment with $H_2O_2$ and the evaporation with $H_2SO_4$ was ignited in a platinum crucible and mixed with eight times its weight of eight parts $KNO_3$ and two parts $K_2CO_3$, the mixture kept at a dull red heat for 30 minutes; the mass was treated with water, the water evaporated off, the residue again treated with water, and the liquid filtered. The residue was dissolved in $H_2O_2$ and HCl, the solution evaporated with $H_2SO_4$, and after dilution poured through a Zn column into $HgCl_2$ solution: no precipitate resulted. The filtrate was strongly acidified with $HNO_3$ and evaporated to dryness; the mass was treated with water, the solution filtered, and the

(white) residue treated with $NH_4OH$; only a small portion of it dissolved, but the solution on acidifying with $HNO_3$ gave a small precipitate of $H_2WO_4$ (1–2 mgm.); the white residue gave no color when heated with $H_2O_2$ and HCl.

The experiment was repeated with a mixture of 300 mgm. W and 300 mgm. Ti: a large gray precipitate was produced in the $HgCl_2$ solution after the $NH_4OH$ precipitate had been fused with $KNO_3$ and $K_2CO_3$.

**G. D., § 5.** — 100 mgm. Ti in one experiment, 5 mgm. Nb in a second, and a mixture of 100 mgm. Ti and 5 mgm. Nb in a third, as oxides, were dissolved in HF, the solution evaporated three times with $HNO_3$, the residue heated 30 minutes at 120°, and then warmed with 10 ccm. 3% $H_2O_2$ and 1 ccm. $HNO_3$ (1.20): the $TiO_2$ and also the mixture of $TiO_2$ and $Nb_2O_5$ dissolved completely; but the pure $Nb_2O_5$ did not seem to dissolve at all.

500 mgm. Ti as $H_2TiO_3$ were dissolved in HF, the solution evaporated just to dryness with $HNO_3$, the residue moistened with $HNO_3$, and the latter evaporated off; 10 ccm. 3% $H_2O_2$ and 2 ccm. HCl (1.12) were added, and the mixture heated to the decomposition-temperature of the $H_2O_2$: in 3 minutes everything had dissolved. — The same experiment was repeated with 2 mgm. Nb as $Nb_2O_5$ and in a separate experiment with 2 mgm. Ta as $Ta_2O_5$: most, if not all, of the substance remained undissolved in each case even on 5–10 minutes' heating. — The experiment was again repeated with a mixture of 12 mgm. Nb and 100 mgm. Ti: everything dissolved on 3 minutes' heating except a few hard flakes, and these went into solution on heating for 5 minutes longer. — It was also repeated with a mixture of 5 mgm. Ta and 100 mgm. Ti: the whole residue went into solution in 5 minutes. It was repeated with 500 mgm. Ti, except that no HCl was at first added with the $H_2O_2$: the residue dissolved much more slowly, and some still remained after 10 minutes; but this dissolved at once on adding 2 ccm. HCl (1.12).

For the separation of titanium and uranium from iron by alkaline $H_2O_2$, see P. H. Walker, *J. Am. Chem. Soc.*, **20**, p. 515 (1898).

To a solution in 5 ccm. $H_2SO_4$ (1.20) of 100 mgm. Ti in one experiment and of 100 mgm. Ti and 6 mgm. Ta in another, 50 ccm. 3% $H_2O_2$ solution were added and this mixture was dropped rapidly from a separating funnel into a cold mixture of 50 ccm. 3% $H_2O_2$ and 15 ccm. $NH_4OH$ (0.90): no precipitate formed within 15 minutes in either case, but a large yellowish white precipitate came out on standing over night at a temperature of about 10°.

**G. D., § 7.** — 100 mgm. Ti as $TiO_4H_4$ were dissolved in 10 ccm. 3% $H_2O_2$ and 2 ccm. HCl (1.12), $SO_2$ gas passed into saturation, $NH_4OH$ added till alkaline, the solution allowed to stand 3 minutes, and then to the mixture a

fourth its volume of HCl (1.20) was added: the whole precipitate dissolved. — The experiment was repeated, substituting 1 mgm. Nb for the 100 mgm. Ti: the $NH_4OH$ precipitate remained in large part undissolved. — The experiment was repeated with a mixture of 50 mgm. Ti and 2 mgm. Nb, and with one of 100 mgm. Ti and 5 mgm. Nb: in the first case, the whole of the $NH_4OH$ precipitate dissolved; and in the second case only a slight one remained, which when dissolved in $H_2SO_4$ and treated with Zn and HCl gave no color, showing the absence of niobium.

**G. D., § 8.** — See C. E., P. 38, N. 4 in regard to the reduction by Zn and the $HgCl_2$ test in the cases of titanium and niobium.

**G. D., § 9.** — To two portions of 7 ccm. $H_2SO_4$ (1.20), $NH_4OH$ was added till alkaline, and then 7 ccm. $(NH_4)_2S$; the mixtures were heated for 30 minutes in a covered casserole, 2 mgm. W as $Na_2WO_4$ were added to each, and each was acidified with $H_2SO_4$ (1.20); to one mixture 3 ccm. 20% $FeCl_3$ solution was at once added, and both mixtures were shaken and filtered: from that to which no $FeCl_3$ was added, a small yellowish pink precipitate separated; while in that to which it was added, a decidedly larger orange-yellow precipitate formed: the filtrate was distinctly yellow in both cases.

**G. D., § 10.** — 300 mgm. W as $Na_2WO_4$, 300 mgm. As as $H_3AsO_4$, 100 mgm. V as $Na_3VO_4$, and 50 mgm. Mo as $(NH_4)_2MoO_4$, in separate experiments, were digested with 10 ccm. $(NH_4)_2S$, the solution precipitated by $H_2SO_4$; the precipitate, sucked as dry as possible, was transferred to a stoppered Erlenmeyer flask, 20 ccm. HCl (1.20) poured over it, and the mixture heated for 20 minutes on a steam bath; the flask was connected by means of tubes passing through the stopper with another flask containing a solution of $Pb(C_2H_3O_2)_2$ strongly alkaline with NaOH, and at the end of the 20 minutes it was removed from the steam bath and a current of air was drawn through the liquid so as to carry the vapors above it into the $Pb(C_2H_3O_2)$ solution: in the cases of the tungsten, arsenic, and vanadium, black precipitates, estimated at 10 mgm., 5 mgm. and 15 mgm. respectively, separated, while in the case of the molybdenum not even a darkening was produced. The acid solution resulting from the action of HCl (1.20) on the $WS_3$ in this experiment was decanted through a filter and evaporated to dryness; 10 ccm. $HNO_3$ (1.20) were added and the mixture heated: a yellow residue estimated at 10 mgm. remained, much of which had already separated during the evaporation of the HCl.

The experiment was repeated with 300 mgm. W, except that HCl (1.12) was used in place of the HCl (1.20): the precipitate of PbS produced seemed to be equal in quantity to that obtained in the preceding test.

300 mgm. W obtained as $WS_3$, as described above, were heated in a flask on a steam bath for 30 minutes with 20 ccm. HCl (1.20), a current of $H_2S$

being passed continuously through the liquid; the solution was filtered and evaporated to dryness, and $HNO_3$ was added: there was a yellow residue not much less in quantity than that obtained when no $H_2S$ was passed in.

**P. 31, N. 2.** — 1 mgm. Sb as $Sb_2O_4$, 1 mgm. Cu as $CuSO_4$, and 1 mgm. Bi as $Bi(NO_3)_3$ were separately dissolved in 5 ccm. 48% HF and 40 ccm. water, and $H_2S$ was passed into the solution in a covered dish for 15 minutes: a considerable precipitate formed in each solution, which was orange-colored in the first case and black in the other cases.

100 mgm. Bi as $Bi(NO_3)_3$ were dissolved in 5 ccm. 48% HF and 40 ccm. water, the solution filtered, the filtrate saturated with $H_2S$, the precipitate filtered out, the filtrate evaporated with $H_2SO_4$, and $NH_4OH$ added: no precipitate resulted.

100 mgm. Se as $SeO_2$ and 100 mgm. Te as $TeO_2$ were separately dissolved in 3 ccm. 48% HF and 24 ccm. water, and $H_2S$ passed into saturation: a large precipitate immediately separated. This was filtered off, the filtrate evaporated to dryness, HCl (1.02) added, and $H_2S$ passed first into the solution in the cold and then into it at a nearly boiling temperature: no more precipitate separated in either case.

500 mgm. $As_2O_3$ were treated with $HNO_3$ (1.42), and the solution evaporated just to dryness; then 3 ccm. 48% HF and 24 ccm. water were added, and $H_2S$ passed in: a precipitate formed only after several minutes, and this continued to increase for an hour. It was then filtered out, and $H_2S$ passed into the filtrate: a large precipitate again resulted.

100 mgm. Mo as $(NH_4)_2MoO_4$ and 4 mgm. W as $Na_2WO_4$ were dissolved in 5 ccm. 48% HF and 40 ccm. water, and $H_2S$ was passed into the cold solution for 30 minutes. The precipitate was treated by P. 43: there was only a scarcely noticeable yellow residue (of $H_2WO_4$) after the evaporation with $H_2SO_4$. The filtrate from the $H_2S$ precipitate was treated by P. 33, 35, 39, 41, omitting the HCl treatment, and P. 43: a fairly large yellow residue (of $H_2WO_4$) resulted.

A mixture of 400 mgm. Mo as $(NH_4)_2MoO_4$, 8 mgm. Sn and 8 mgm. W in HF solution was dissolved in 5 ccm. 48% HF and 40 ccm. water; 2 ccm. $H_2SO_4$ (1.84) were added, and $H_2S$ was passed for 30 minutes into the cold solution; the precipitate was treated by P. 41, 42, and 43, and the filtrate by the usual complete procedure: the $HgCl_2$ test obtained by treating the precipitate was only about one-fourth as large as that obtained by treating the filtrate; no tungstic acid separated in the analysis of the precipitate, while a large quantity was obtained in that of the filtrate upon treating the ignited sulphide with $HNO_3$ and $H_2SO_4$.

300 mgm. Mo as $(NH_4)_2MoO_4$ were dissolved in 5 ccm. 48% HF and 40 ccm. water, $H_2S$ passed into the cold solution for 30 minutes, and the mixture filtered: a large black precipitate resulted, and the filtrate became

very turbid on short standing. The filtrate was placed on a steam bath and $H_2S$ passed into the hot solution for 30 minutes more and filtered: a much smaller precipitate was obtained than before. This last precipitate was treated with $HNO_3$ (1.20), and the solution was filtered; the residue was ignited, and the filtrate from it evaporated, the two residues united, heated to a low red heat, and weighed: 39 mgm. of $MoO_3$ corresponding to 26 mgm. Mo were obtained. The filtrate from the second $H_2S$ precipitate was evaporated, and the residue ignited and weighed: 45 mgm. $MoO_3$ corresponding to 30 mgm. Mo were obtained. This shows that of the 300 mgm. present only 56 mgm. remained unprecipitated after the first 30 minutes' treatment with $H_2S$ in the cold.

The last experiment was repeated, except that 3 ccm. $H_2SO_4$ were added to the HF solution before passing in $H_2S$, and except that no quantitative determinations were made: the two precipitates obtained were of nearly the same size as before.

500 mgm. Sn as metal were treated with $HNO_3$ (1.42) and the latter evaporated off; the residue was dissolved in 5 ccm. 48% HF and 40 ccm. water, and $H_2S$ passed into the cold solution for over an hour; no precipitate appeared.

500 mgm. W as $Na_2WO_4$ were dissolved in 3 ccm. HF and 24 ccm. water, and the cold solution was treated with $H_2S$ gas for an hour: no precipitate separated.

A mixture of 500 mgm. Sb and 2 mgm. Sn as metals was treated with $HNO_3$, the mixture evaporated, the residue dissolved in 48% HF, the solution diluted with eight times its volume of water and treated with $H_2S$ gas for 30 minutes; the precipitate next filtered out, the filtrate evaporated with 3 ccm. $H_2SO_4$, and the solution diluted and treated with granulated zinc and a piece of platinum, as long as gas evolution continued; then to the mixture strong HCl was added and heat applied till the zinc was all dissolved, and the solution was filtered and added to $HgCl_2$: a small white precipitate, which turned black on treatment with $NH_4OH$, resulted. — The experiment was repeated with 500 mgm. Sb and 1 mgm. Sn: no precipitate of HgCl was obtained.

5 ccm. 48% HF and 40 ccm. water were saturated cold with $H_2S$ and kept so, while portions of 1 mgm. Pb as $Pb(NO_3)_2$ were added till a permanent precipitate resulted: 6 mgm. Pb were required.

**P. 31, N. 3.** — 1 mgm. Sb as $Sb_2O_5$ was dissolved in 5 ccm. 48% HF and 25 ccm. water, and $H_2S$ passed in at the room temperature for 30 minutes: no precipitate formed. The solution was then cooled in ice water, and $H_2S$ again passed: a distinct precipitate separated. The mixture was heated till the precipitate redissolved, then cooled to room temperature, again saturated with $H_2S$ (whereby no precipitate was produced), diluted

with 15 ccm. water and again saturated with the gas: a distinct precipitate resulted.

500 mgm. Sb as metal were treated with $HNO_3$, the acid evaporated, the residue dissolved in 5 ccm. 48% HF and 40 ccm. cold water, $H_2S$ passed in half an hour, the precipitate filtered out, the filtrate evaporated to fuming with 1 ccm. $H_2SO_4$, diluted with water (whereupon a large white precipitate separated), and $H_2S$ passed into saturation: an orange precipitate not very different in quantity from that that separated from the HF solution was obtained.

A solution of 500 mgm. Sn as $SnO_2$ and 1 mgm. Sb in 5 ccm. 48% HF and 40 ccm. water was saturated with $H_2S$ in the cold: a decided orange-colored precipitate separated.

1 mgm. Sb was dissolved in a mixture of 5 ccm. 48% HF, 40 ccm. water, and 1 ccm. $H_2SO_4$ (1.84), and $H_2S$ was passed into saturation in the cold: no precipitate formed. — The experiment was repeated with 2 mgm. Sb: a distinct, compact, orange precipitate separated.

2 mgm. As as $As_2O_5$ were dissolved in 5 ccm. 48% HF and 40 ccm. water, and $H_2S$ passed into the cold solution for 50 minutes: no precipitate whatever separated. The solution was then heated on a steam bath, and $H_2S$ again passed in: a precipitate appeared almost immediately.

A mixture of 400 mgm. Mo as $(NH_4)_2MoO_4$, 2 mgm. Ta, 2 mgm. Ti, 2 mgm. Sn, and 4 mgm. W, dissolved in 5 ccm. 48% HF and 40 ccm. water, was treated with $H_2S$, first cold and then hot: the solution became very dark-colored, but very little precipitate separated. Then 3 ccm. $H_2SO_4$ (1.84) were added: a very bulky, slimy precipitate instantly separated, causing the solution almost to gelatinize. The mixture was filtered: the liquid ran through with extreme slowness. The filtrate was tested by the complete procedure for all of the elements present in small quantity: no test for any of them except tantalum was obtained, indicating that they were carried down by the slimy precipitate.

**P. 33, N. 2.** — 100 mgm. dehydrated $H_2SiO_3$ were dissolved in HF, $H_2SO_4$ was added, and the solution was evaporated to complete dryness: no residue could be seen, showing that one evaporation with HF and $H_2SO_4$ suffices to expel all the silica.

**P. 33, N. 4.** — 500 mgm. Sn as $H_2SnO_3$, 300 mgm. Ti as $H_2TiO_3$, 100 mgm. Nb as $Nb_2O_5$, 100 mgm. Ta as $Ta_2O_5$, and 500 mgm. Mo as $MoO_3$ were dissolved in separate experiments in a little HF, 2–3 ccm. $H_2SO_4$ (1.84) were added, the solution was evaporated till it fumed strongly, and then after cooling it was poured gradually into 5 ccm. cold water: no permanent precipitate separated in any case; the molybdenum solution had a deep blue color, and before dilution there were blue spots above the surface of the liquid. The experiment was repeated with 100 mgm. Nb,

and with 100 mgm. Ta, taking no especial care to cool the $H_2SO_4$ upon dilution: a large, white flocculent precipitate separated in each case.

To 2 mgm. W were added 2 ccm. HF, 0.5 ccm. $HNO_3$, and 3 ccm. $H_2SO_4$; the solution was heated gently until most of the HF was expelled; it was then heated at 110° in a hot closet for 30 minutes; and finally it was added to 8 ccm. water: a precipitate separated almost immediately.

The experiment was repeated, except that the mixture was heated on a sand bath just below the fuming point for 30 minutes: upon dilution a precipitate began to separate.

To 2 mgm. W and 4 mgm. W as $Na_2WO_4$, 2 ccm. $H_2SO_4$ (1.84) were added, and the solution evaporated to the fuming point: even after cooling, the solution remained clear. The liquid was added to 5 ccm. water: a white turbidity appeared in 3–5 minutes in the 4 mgm. portion, and in 30 minutes in the 2 mgm. portion; on standing over night, yellow precipitates had settled out in both cases. The experiment, with some variations, was many times repeated with 1 mgm. W: in no case did any precipitate separate, even on standing.

100 mgm. W as $Na_2WO_4$ were dissolved in a little water, 1 ccm. $H_2SO_4$ (1.84) added, and the mixture evaporated to the fuming point: a large quantity of a heavy, yellow powder separated.

**P. 34, N. 3.** — 0.1 mgm. $PO_4$ as $Na_2HPO_4$ was added to 5 ccm. of the $(NH_4)_2MoO_4$ reagent, and the mixture was warmed: a considerable yellow precipitate formed at once.

**P. 35, N. 2.** — To 300 mgm. Mo as $(NH_4)_2MoO_4$, 300 mgm. W as $Na_2WO_4$, and 300 mgm. V as $Na_3VO_4$ in separate experiments, 10 ccm. water, 3 ccm. $NH_4OH$, and 10 ccm. $(NH_4)_2S$ were added, and the mixture kept at 50°–60° for 45 minutes; everything stayed in solution in the case of the molybdenum and tungsten; a rather small green precipitate remained in the case of the vanadium; the molybdenum had a deep orange-red color, the vanadium a yellow-brown color. The experiment was repeated with 1 mgm. Mo: a distinct orange color was apparent.

Three portions of 500 mgm. Sn as metal were treated with three portions of 5 ccm. $HNO_3$ (1.42), to one of which had been added 500 mgm. V as $Na_3VO_4$, to another 500 mgm. W as $Na_2WO_4$, and to the third 500 mgm. Mo as $(NH_4)_2MoO_4$. The mixture was evaporated to dryness, the residue heated for 1 hour at 120°, and then treated by P. 5, 6, 33 and 35: on adding an excess of $NH_4OH$, nothing remained undissolved in the mixture containing vanadium, there was a yellowish white precipitate in that containing tungsten, and a grayish blue one in that containing molybdenum. On adding 10 ccm. cold $(NH_4)_2S$, the mixtures containing vanadium and molybdenum became deep red, and no precipitate remained; in that containing tungsten, everything also dissolved.

A solution of 300 mgm. Ti and 5 mgm. W in HF was treated by P. 33, 35, 36, and the first paragraph of P. 38: a decided white precipitate was produced in the $HgCl_2$ solution, showing the presence of tungsten in the (well-washed) $(NH_4)_2S$ precipitate. The experiment was repeated with many other mixtures of titanium and tungsten, with the same result.

As to the impossibility of completely removing tin and tungsten from niobium and tantalum with $(NH_4)_2S$, see Hall, "Observations on the Metallic Acids," thesis submitted to University of Pennsylvania, p. 9 (1904).

A mixture of 400 mgm. Ti and 200 mgm. Mo was dissolved in HF and treated by P. 33 and 35, the precipitate being three times washed with hot water upon the filter with the help of suction: it still had a strong orange color. It was returned to a casserole and heated with frequent stirring upon a water bath with 10 ccm. $NH_4OH$ (0.90) and 40 ccm. water; the precipitate was then filtered out and washed: it now had only a slight yellowish color. It was dissolved in HF and treated by the whole of P. 38: a large precipitate was obtained in the first $HgCl_2$ test, but none whatever in the second $HgCl_2$ test after the fusion with $Na_2CO_3$ and S, showing that the quantity of molybdenum retained in the $(NH_4)_2S$ precipitate after digestion with $NH_4OH$ is not so great that it cannot be removed by the fusion. — The experiment was repeated, except that the $(NH_4)_2S$ precipitate was only well washed with water, not digested with $NH_4OH$: in this case a large precipitate was obtained in the $HgCl_2$ test, even after the fusion with $Na_2CO_3$ and S, showing that the digestion with $NH_4OH$ may be necessary.

**P. 36, N. 2.** — 100 mgm. Ti as $H_2TiO_3$ and 100 mgm. Nb as $Nb_2O_5$, in separate experiments, were dissolved in HF and treated by P. 33, 35, and 36: the whole $H_2TiO_3$ precipitate dissolved in the $H_2O_2$, and of the $HNbO_3$ not more than 1 mgm. remained undissolved. The experiment was several times repeated with 300 mgm. Ti as $H_2TiO_3$: in every case a large white precipitate, amounting to from one-third to one-sixth of the original quantity, remained undissolved. This precipitate was treated successively with two fresh portions of $H_2O_2$ and HCl: each time the liquid was strongly colored, but there was still a large residue. This residue was treated with 5 ccm. cold HF; it dissolved completely in 2 or 3 minutes.

20 mgm. Ta as $Ta_2O_5$ were dissolved in HF, and the solution treated by P. 33, 35, and 36; the $H_2O_2$ solution was saturated with $SO_2$ and $NH_4OH$ added: a precipitate about equal in amount to the residue undissolved by the $H_2O_2$ was produced. This residue was dissolved in HF and again treated by P. 33, 35, and 36, and the $H_2O_2$ solution was saturated with $SO_2$ and made alkaline with $NH_4OH$: again a precipitate nearly equal in amount to the residue was obtained.

1 mgm. Ta as $Ta_2O_5$ in HF solution was treated by P. 33, 35, 36,

and 37, and the $H_2O_2$ solution obtained in P. 36 was saturated with $SO_2$ and made alkaline with $NH_4OH$: about one-half the $(NH_4)_2S$ precipitate dissolved in the $H_2O_2$, and from the residue a distinct precipitate of $K_2TaF_7.Ta_2O_5$ was obtained by P. 37.

300 mgm. Sn and 300 mgm. Ti in HF solution were treated by P. 33, 35, and 36: there was a large residue insoluble in $H_2O_2$ and HCl. This was removed from the filter and warmed with 48% HF: a large residue still remained. This was fused with $Na_2CO_3$ and S and treated with hot water: the mass dissolved completely, showing the absence of much titanium. The solution was tested for tin by P. 39, 41 (omitting the ignition), and 43: a very large precipitate of HgCl resulted.

**P. 36, N. 3.** — Two portions of 20 mgm. Ti in HF solution were evaporated with 2 ccm. $H_2SO_4$ (1.84), the solution diluted with 5 ccm. water and a large excess of $NH_4OH$, and heated on a steam bath for 1 hour; the precipitates were filtered off, washed, and transferred to test tubes; to one of them 10 ccm. hot 3% $H_2O_2$, and to the other a hot mixture of 10 ccm. 3% $H_2O_2$ and 2 ccm. HCl (1.12), were added, and the mixtures shaken for 2 minutes: in the first case, much of the precipitate was undissolved and the mixture had a light yellow color; in the second case, a clear, deep orange-red solution resulted.

**P. 36, N. 4.** — 0.1 mgm. Ti and 100 mgm. Ti were added to 10 ccm. $H_2O_2$ and 2 ccm. HCl (1.12): a distinct yellow color resulted in the first case, and a deep orange-red in the second.

**P. 36, N. 5.** — 5 mgm. V and 20 mgm. V as $Na_3VO_4$ were added to 10 ccm. 3% $H_2O_2$ and 2 ccm. HCl (1.12): an orange-yellow color resulted in the first case and a deep orange-red in the second. The experiment was repeated with 5 mgm. W as $Na_2WO_4$: no color was produced. It was repeated with 5 mgm. Mo and with 100 mgm. Mo as $(NH_4)_2MoO_4$: a very pale yellow color, not so strong as that produced by 0.1 mgm. Ti, resulted in the first case, and a deep, pure yellow color in the second case.

**P. 37, N. 2.** — 1 mgm. Ta as $Ta_2O_5$ and 10 mgm. $SiO_2$ were dissolved in HF, and, omitting the usual evaporation with $HNO_3$, $K_2CO_3$ was immediately added, the solution was evaporated, the residue heated and dissolved in a little water, and the solution boiled down to 1 ccm.: no precipitate separated, even on standing.

**P. 37, N. 3.** — For the solubility and composition of the potassium fluotantalate and fluoxytantalate, see Marignac, *Ann. chim. phys.* (4), 9, pp. 268, 269 (1866).

A portion of 2 mgm. Ta was treated by P. 37, and two other portions of 2 mgm. Ta were treated in the same way except that the residue, after adding $K_2CO_3$ and evaporating, was in one case heated only till it became dry (but not enamel white), and was in the other case heated to redness: scarcely any

precipitate formed in the portion heated only to dryness, a fairly large precipitate of the usual appearance separated in that treated exactly according to the procedure, and a lighter, more bulky, powdery one resulted in the portion heated to redness.

**P. 37, N. 4.** — For the solubility of $K_2TiF_6$, see Marignac, *Ann. chim. phys.* (4), **8**, p. 65 (1866).

**P. 37, N. 5.** — 100 mgm. Nb as $HNbO_3$, precipitated from $H_2SO_4$ solution by $NH_4OH$, were dissolved in HF and treated by P. 37: at the end a large, granular precipitate separated in the cold when the volume was 1.5 ccm., but this dissolved on heating; and after 1 ccm. more of water was added, it remained in solution even after cooling.

The experiment was repeated with a mixture of 100 mgm. Nb and 1 mgm. Ta: at the end, when the volume was 1 ccm., the large, granular precipitate separated as before, and this dissolved when 3 ccm. water were added, but there then remained a small quantity of the heavy, dirty white precipitate characteristic of tantalum.

For the solubility and composition of the potassium fluoxyniobate, see Marignac, *Ann. chim. phys.* (4), **8**, p. 28 (1866).

**P. 38, N. 3.** — Direct experiments confirmed all the statements in regard to the colors produced.

**P. 38, N. 4.** — Reduction of $TiO_2$ by zinc to $Ti_2O_3$, see König and v. d. Pfordten, *Ber. chem. Ges.*, **22**, p. 2079 (1889).

Reduction of $Nb_2O_5$ by zinc to $Nb_2O_3$, see Osborne, *Am. J. Sci.* (3), **30**, p. 333 (1885).

1 mgm. Nb as $Nb_2O_5$, a mixture of 2 mgm. Nb and 100 mgm. Ti, and one of 1 mgm. Nb and 100 mgm. Ti were, in separate experiments, dissolved in HF, 1 ccm. $H_2SO_4$ (1.84) added, and the mixture evaporated till the acid fumed; the solution was then treated with HCl and Zn, and tested with $HgCl_2$ by P. 25: a distinct, silky, white precipitate formed immediately in each case.

The experiment was repeated with 100 mgm. Ti, 10 mgm. Ta (previously freed from niobium by precipitation as $2K_2TaF_7.Ta_2O_5$), and with 100 mgm. Sn as oxides and with 300 mgm. Zr as $Zr(SO_4)_2$ in separate experiments: in every case the $HgCl_2$ solution remained perfectly clear. The experiment was several times repeated with 300 mgm. Ti as $H_2TiO_3$ from three different commercial sources: no precipitate formed at once or for a few minutes in the $HgCl_2$ solution, but a turbidity always appeared in 15 minutes, and this increased on longer standing.

The experiment was repeated with 100 mgm. Mo as $(NH_4)_2MoO_4$, with 100 mgm. V as $Na_3VO_4$, and with 4 mgm. W as $Na_2WO_4$ in separate experiments: a large precipitate was produced in the $HgCl_2$ solution in each case.

For evidence of the reduction of $WO_3$ to $WO_2$, see v. d. Pfordten, *Ber.*

*chem. Ges.*, **16**, p. 508 (1883); of $MoO_3$ to $MoO_2$ (when air is not completely excluded), see v. d. Pfordten, *Ber. chem. Ges.*, **15**, pp. 1925–1929 (1882); of $V_2O_5$ to $V_2O_3$, Roscoe, *Ann. Chem. Suppl. Bd.*, **6**, p. 94 (1867). The color changes are also there described.

Mixtures of 300 mgm. W and 300 mgm. Ti, of 5 mgm. W and 300 mgm. Ti, and of 300 mgm. Ti and 300 Mo, in separate experiments, were dissolved in HF and treated by P. 33, 35, 36, and 38: in every case a rather large precipitate was produced when the third of the solution was treated with Zn and tested with $HgCl_2$. After the fusion of the remainder with $Na_2CO_3$ and S, the second test with Zn and $HgCl_2$ resulted in no immediate precipitate in the case of the last two of these mixtures, and in a slight turbidity (less than that given by 1 mgm. Nb) in the first mixture. The experiment with this first mixture was repeated with the same result.

2 mgm. Nb and 200 mgm. Ti in one experiment and 2 mgm. Nb alone in another were dissolved in HF, evaporated with 2 ccm. $H_2SO_4$ (1.84) and treated by the last paragraph of P. 38: a considerable precipitate of HgCl was obtained in each case, that with the niobium alone being smaller, probably owing to difficulties of manipulation in the process. But in some of the test analyses (see the next chapter), 2 mgm. Nb disappeared between the first and second tests with $HgCl_2$ in the processes connected with the fusion.

**P. 38, N. 5.** — A mixture of 300 mgm. Ti as $H_2TiO_3$ and 5 mgm. W as $Na_2WO_4$ in HF solution was treated by P. 33 and 35. The $(NH_4)_2S$ filtrate was then acidified with $H_2SO_4$ (1.20), the precipitate tested for tungsten by P. 43; and the filtrate by P. 40: no precipitate (of $H_2WO_4$) was obtained in either case. The $(NH_4)_2S$ precipitate was then fused with $Na_2CO_3$ and S and the fused mass treated with water as in P. 38; the aqueous solution was acidified with $H_2SO_4$ (1.20), and the precipitate tested by P. 43, and the filtrate by P. 40: no precipitate of $H_2WO_4$ resulted from the treatment of the $H_2SO_4$ precipitate; but a small, though very distinct, compact yellow residue was obtained from the filtrate. The residue from the $Na_2CO_3$ and S fusion that was insoluble in water was dissolved in HF by a half-hour's digestion, and treated by the first paragraph of P. 38: no precipitate of HgCl was obtained, showing that the tungsten had been completely separated from the titanium by the $Na_2CO_3$ and S fusion.

For the complete separation of tin and tungsten from niobium and tantalum by fusion with $Na_2CO_3$ and S, see Hall, "Observations on the Metallic Acids," thesis submitted to the University of Pennsylvania, p. 9 (1904).

**P. 39, N. 1.** — To two portions of 7 ccm. $H_2SO_4$ (1.20), $NH_4OH$ was added till alkaline, and then 7 ccm. $(NH_4)_2S$, and the mixtures were heated at 50°–60° for 30 minutes. To one of the mixtures 2 mgm. W as $Na_2WO_4$

were added, and both were acidified with $H_2SO_4$ (1.20) and filtered: a small pink precipitate was obtained from both solutions; but the filtrate from the blank was colorless, while that from the solution containing tungsten was of a pronounced yellow color. — The experiment was twice repeated, using 1 mgm. in place of 2 mgm. W: a bright yellow precipitate formed on adding the $H_2SO_4$, and the filtrate was distinctly yellow.

A mixture of 6 gm. of $Na_2CO_3$ and S with 1 mgm. W, in one case, and 6 gm. of $Na_2CO_3$ and S alone in another, were fused for 15 minutes, and the fused masses dissolved in water, and the solutions filtered, acidified with $H_2SO_4$ (1.20), shaken, and again filtered: the mixture containing tungsten gave a yellowish pink precipitate and a slightly yellow filtrate; the blank gave a pale yellow precipitate and a colorless filtrate.

5 mgm. W as $Na_2WO_4$ were treated by P. 33, 35, and 39: the precipitate was of a bright yellow color, much deeper than that of precipitated S; the filtrate was deep yellow. The precipitate was ignited, the residue fused with $Na_2CO_3$, the mass dissolved in water, and the solution boiled with $HNO_3$: a small, but unmistakable, yellow precipitate of $H_2WO_4$ was obtained. The filtrate was treated by P. 40: a large yellow precipitate, about ten times as great as that from the $H_2SO_4$ precipitate, remained.

In regard to the incomplete precipitation of $WS_3$ by acids from solutions in alkaline sulphides, see also Jannasch and Bettges, *Ber. chem. Ges.*, **37**, p. 2223 (1904).

A mixture of 300 mgm. Sn and 2 mgm. W was treated by P. 33 and 35, and the $(NH_4)_2S$ filtrate by P. 39: the filtrate was colorless. This filtrate was treated by P. 40: a small but unmistakable yellow precipitate of $H_2WO_4$ resulted.

The experiment was repeated with a mixture of 300 mgm. Sn and 10 mgm. W: a yellow precipitate estimated at 1 mgm. W was obtained from the filtrate.

A mixture of 30 mgm. Sn as $SnCl_4$, 8 mgm. W as $Na_2WO_4$ and 20 mgm. $PO_4$ as $Na_2HPO_4$ was treated by P. 35, 39, 40, 41, 43, and 44, and the HCl solution of the ignited sulphides obtained in P. 41 was divided, part being evaporated with $HNO_3$ and tested with $(NH_4)_2MoO_4$, and the remainder evaporated to a small volume, diluted, treated hot with $H_2S$, filtered, and the filtrate concentrated and tested for tungsten with Zn: no indication of tungsten was obtained either at this last point or in P. 43 or 44; but a strong blue color resulted at the end of P. 40. Phosphate was present in considerable quantity in the HCl solution, though the sulphide precipitate had been thoroughly washed; also, of course, in large quantity in the $H_2SO_4$ filtrate.

To a mixture of 200 mgm. Mo as $(NH_4)_2MoO_4$ and 2 mgm. W as $Na_2WO_4$, and to one of 400 mgm. Mo and 4 mgm. W in $H_2SO_4$ solution,

were added $NH_4OH$ and 10 ccm. $(NH_4)_2S$, and the deep orange-red solution digested at 50° for 30 minutes, and then treated by P. 39: there resulted a black precipitate and a filtrate which was colorless with the first mixture, pale blue from the second. The filtrate was treated by P. 40: no precipitate of $H_2WO_4$ remained in either case. That from the second mixture was also tested with Zn and KSCN: a pronounced but not very strong red color resulted.

In certain test analyses, however, where molybdenum and tungsten were both present, the latter was found only in the filtrate, and there in large quantity (see T. A., 34, 36).

1 mgm. Mo and 1 mgm. Sn in $H_2SO_4$ solution were separately digested with 10 ccm. $(NH_4)_2S$, and the solution acidified with $H_2SO_4$: a dark brown or yellowish brown precipitate separated, and the filtrate was colorless. The filtrate from the $MoS_3$ was evaporated to a volume of 3 ccm., and Zn and KSCN added: no coloration was produced.

100 mgm. V as $Na_3VO_4$ were digested with $(NH_4)_2S$ as in P. 33 and 35, the small bluish gray precipitate remaining was filtered out, and the filtrate treated with $H_2SO_4$ by P. 39: a large brown precipitate and pale blue filtrate resulted, showing that the vanadium was divided.

**P. 40, N. 3.** — 1 mgm. W and 50 mgm. $PO_4$ as $Na_2HPO_4$ were added to 5 ccm. HCl (1.06) and Zn added: a pronounced blue color resulted.

**P. 41, N. 1.** — The experiment first described under C. E., G. D., § 10 was repeated with 300 mgm. W as $WS_3$, with 100 mgm. V as $V_2S_5$, and with 100 mgm. Mo as $MoS_3$ in separate experiments, except that the sulphides were ignited in a $H_2S$ atmosphere, as directed in P. 41, before heating with the HCl (1.20), the crucible being heated without a jacket over a powerful burner: there was no darkening whatever of the $Pb(C_2H_3O_2)_2$ solution in any of the three cases.

300 mgm. Sn obtained as $SnS_2$ by acidifying an $(NH_4)_2S$ solution were treated by P. 41, the crucible being heated within a burnt-clay jacket for 10 minutes with the full flame of a powerful burner: almost the whole mass (which was black and glistening) dissolved in the hot HCl (1.20), there being only a very small yellow residue. This residue was washed and treated with $HNO_3$ and HCl, the solution evaporated twice with $HNO_3$, and the residue treated with $HNO_3$ (1.20): only a small turbidity remained.

This experiment was repeated except that the crucible was heated without a jacket and only to a low red heat: the ignited mass was mostly yellowish, but contained some black particles, and it left a large residue of yellow scales with metallic lustre when boiled with HCl (1.20).

This experiment was repeated except that the crucible was heated without a jacket to the highest temperature obtainable with a powerful burner: it was 30 minutes before the whole mass became black; after boiling with HCl

(1.20) for 20 minutes, there was still a considerable quantity of a yellow, scaly residue.

A mixture of 300 mgm. Sn and 3 mgm. W, and one of 300 mgm. Sn and 1 mgm. W, obtained as sulphides by adding $H_2SO_4$ to a $(NH_4)_2S$ solution, were treated by P. 41 and 43: a considerable yellow residue of $H_2WO_4$ was obtained in the first case, and a small but unmistakable one in the second case.

200 mgm. Sb as precipitated $Sb_2S_5$ were treated by P. 41 and 42: the ignited mass consisted of a black button, and this dissolved completely in the HCl (1.20) upon boiling for 5 minutes.

**P. 42, N. 1.** — 1 mgm. Sn as precipitated $SnS_2$ was treated by P. 41 and 42, the ignition being continued for 25 minutes: a considerable precipitate of HgCl was produced.

Separate mixtures of 300 mgm. W as $Na_2WO_4$ with 1 mgm. Sn, 2 mgm. Sn, 4 mgm. Sn (in two experiments), and 10 mgm. Sn as $SnCl_4$ were treated with $NH_4OH$ and $(NH_4)_2S$, and then by P. 39 and 41, and the HCl solution was then immediately added to $HgCl_2$ solution: no precipitate was produced in the first three cases (with 1–4 mgm. Sn), but a fairly large one resulted in the last case (with 10 mgm.). The experiment was repeated with a mixture of 300 mgm. W and 1 mgm. Sn, but the HCl solution was treated by P. 42: a distinct residue of Sn and a decided precipitate of HgCl resulted.

The HCl solutions obtained in the experiments described under P. 41, N. 1, by heating on a steam bath 300 mgm. W as ignited $WS_2$, 100 mgm. V as ignited $VS_2$, and 100 mgm. Mo as ignited $MoS_2$, with HCl (1.20), were added to $HgCl_2$ solution: not even a cloudiness resulted in any of the cases. The HCl solution obtained by boiling the ignited $Sb_2S_3$ with HCl (1.20) was added to $HgCl_2$ solution: a large precipitate (of $SbO_3H_3$) separated, but this dissolved completely upon adding HCl.

**P. 43, N. 1.** — 300 mgm. Mo obtained as $MoS_3$ by precipitation from $(NH_4)_2S$ solution by $H_2SO_4$ were boiled with 10 ccm. $HNO_3$ (1.10): apparently all the molybdenum went into solution. The residue was washed and treated repeatedly with a portion of $NH_4OH$; the solution was acidified with HCl and treated with Zn and KSCN: no red coloration appeared.

A mixture of 2 mgm. W and 500 mgm. Mo in HF solution was treated by P. 3, 5, 6, 33, 35, 39, and 43: an unmistakable precipitate of $H_2WO_4$ was obtained.

100 mgm. Mo and 100 mgm. V as ignited sulphides were separately warmed on a steam bath with 8 ccm. $HNO_3$ (1.42) and 2 ccm. HCl (1.20): in 2 minutes the residue dissolved completely. The molybdenum solution was evaporated to 3 ccm.: a large precipitate separated.

The experiment was repeated with 300 mgm. W as ignited $WS_2$: the black residue was completely converted into a yellow one within 5 minutes.

In regard to the difficulty of separating $H_2WO_4$ completely by the addition of strong acid to a tungstate solution, see Jannasch and Bettges, *Ber. chem. Ges.*, **37**, p. 2225 (1904).

**P. 43, N. 2.** — Mixtures of 2 mgm. W as $Na_2WO_4$ and 100 mgm. Mo as $(NH_4)_2MoO_4$ (in two experiments) and of 4 mgm. W and 100 mgm. Mo were treated by P. 35, 39, 40, 41, and 43: no precipitate of $H_2WO_4$ was obtained in any case from the $H_2SO_4$ filtrate tested by P. 40; and no precipitate separated from the $HNO_3$ and HCl solution of the ignited sulphides even on standing over night; but upon evaporating this solution with $H_2SO_4$, a large yellow residue separated from the mixture containing 4 mgm. W, an extremely small but distinct one from one of those containing 2 mgm. W, and nothing whatever from the other containing 2 mgm. even on standing over night.

**P. 44, N. 1.** — 0.5 mgm. W as $Na_2WO_4$ was added to 2 ccm. HCl (1.12) and a few granules of zinc introduced: a strong blue coloration appeared almost immediately, and in a few minutes blue flocks separated from the liquid. The color persisted for at least 15 minutes. The experiment was repeated with 2 mgm. W: an intensely blue flocculent precipitate separated, and on filtration the mixture yielded a perfectly colorless filtrate.

To 10 mgm. Mo and 100 mgm. Mo as $(NH_4)_2MoO_4$, dissolved in a few drops of water, 2 ccm. HCl (1.12) and a few granules of zinc were added: in each case the solution became yellow at once, then dark orange-yellow, next dark green, and finally dark olive brown, but no precipitate formed except after long standing; at no time was a blue coloration noticeable.

100 mgm. Mo as $(NH_4)_2MoO_4$ were dissolved in 10 ccm. water and 0.5 ccm. HCl (1.12) added: the solution soon assumed a clear blue color, which became deep blue after some minutes.

CONTRIBUTIONS FROM THE LABORATORY OF SANITARY CHEMISTRY.

VI.

# *THE EXACT ESTIMATION OF ATMOSPHERIC CARBON DIOXIDE: A BRIEF SURVEY.*

BY A. G. WOODMAN.

TREATISES on chemistry almost invariably contain in the text the following statement, which has become classical and, it might almost be said, official: *The atmosphere contains a small quantity of carbonic acid, varying ordinarily between four and six ten-thousandths in volume.*

This dictum of past chemical authority we now know to be untrue, but the question of the true amount of atmospheric carbon dioxide has been, in a certain measure, so difficult, and its determination has required so much labor and thought, that it has seemed of interest to present briefly a historical sketch of the development of chemical knowledge in this respect.

The existence of carbon dioxide in the air was first demonstrated by Dr. Black, of Edinburgh, probably between 1752 and 1754. In his "Lectures"[1] he says: "When this fluid (lime water) is exposed to the open air, the particles of lime which are at the surface gradually attract fixed air which is mixed with the atmosphere. . . . It was evident that the sort of air with which the lime is disposed to unite is a particular species, which is mixed in a small quantity only with the air of the atmosphere. To this particular species I gave the name of fixed air."

The elder De Saussure, in his observations on the summit of Mont Blanc, exposed strips of paper moistened with caustic potash solution to the air for one and a half hours and found that when dry they effervesced briskly with acids.

Alexander von Humboldt (1797) was probably the first chemist who undertook the exact determination of the amount of atmospheric

[1] Lectures on the Elements of Chemistry. By Joseph Black, M.D., Edinburgh, 1803.

carbon dioxide, and since his time the problem has engaged the attention of many chemists, the *Journal of the London Chemical Society* alone containing over 120 references to the subject. Many of the results obtained, viewed in the light of later-day knowledge, seem most strange; the conflict of opinion has at times been extreme; and the endeavor to simplify the requisite apparatus on one hand and to increase the accuracy of the results on the other has led to some rather amusing propositions.

This may be illustrated briefly by one or two examples taken from the literature. The volume of air considered necessary for the determination varies from the 30-cubic-centimeter bottle of Haldane to the enormous 600-liter aspirator of Reiset, which was mounted on a cart and drawn about by a horse from place to place. Even for a given sample of air of definite volume, opinions differ greatly as to the time and labor necessary to collect it. Lebedinzeff, for example, considers it necessary to aspirate 200 liters of air through a bottle of 8 liters capacity in order to effect a complete exchange of the air, while Dr. Gill finds it sufficient to fill the bottle four times by fifteen strokes of a pair of bellows. One of the early investigators, De Saussure, collected the air in a glass balloon having a capacity of about 45 liters, and absorbed the carbon dioxide by means of barium hydroxide. In order to ensure the complete absorption he allowed the solution to remain in contact with the air for *two months*. At length De Saussure became convinced that so long a time was unnecessary, and the time was finally reduced to *one hour*. Other methods which have been seriously proposed are obviously inaccurate or impracticable. Dr. Notter, who contributes the article on air in Stevenson and Murphy's standard work on hygiene, says: "Perhaps the best plan is to fill a jar with clean water and empty it in that part of the air space it is desired to examine, taking care to allow it to drain." The capacity of the bottle is given as 1 gallon; it is obviously impossible to remove all of the water by draining, yet no allowance is made for it in the subsequent titration. The error thus introduced is about 20 per cent., and for most hygienic determinations it would seem better to make use of one of the simpler but equally accurate methods than one which needs the help of an express wagon in its execution. Dr. Louis Parkes[1] recommends the use of a 2-liter glass-stoppered bottle, which is to be filled with mercury and emptied at the point where

[1] Manual of Hygiene, 2d ed., p. 260.

it is desired to collect the air. To even the most casual observer it will be apparent that 50 pounds of mercury is too much to carry about comfortably, to say nothing of the increased danger of contaminating the sample by the greater amount of exertion and labor necessary to collect it. Symonds and Stephens, wishing to go into a crowded police court and collect samples of air within a few feet of the magistrate without attracting attention, speak of carrying several liter bottles in their pockets and 2-liter bottles under a mackintosh. While the writer does not wish to deny the possibility of thus collecting samples, his experience in securing air samples in a crowded theater, where it was necessary to avoid attracting attention, leads to the fear that the attention of persons near the collectors was not wholly devoted to the business of the court. Considerable experience leads to the conclusion that the rapid and easy collection of air samples in public places is a problem not yet satisfactorily solved.

But apart from the amusing side, a vast amount of serious consideration has been given to the subject, the extent of which may perhaps best be comprehended by a brief review of the work of some of the more important investigators in the field.

Since the earliest crude attempts, all chemical methods have been based on the absorption of carbon dioxide by alkalies and alkaline earths. It may be the diminution in volume through the absorption of the carbon dioxide that is measured; the carbon dioxide may be separated as barium carbonate and weighed; the reduced alkalinity of the absorbing solution may be determined; the carbon dioxide may be set free from the absorbing solution and its volume determined directly. All of these methods have been used with more or less success. For a general review they may be divided into two groups: (1) those in which a definite volume of air is taken for the analysis, and (2) those in which a large volume of air is aspirated through the apparatus. Each division includes several classes.

Group I. (*a*) *Eudiometric.* — The direct measurement of the diminution in volume of the air through absorption of the carbon dioxide has been employed by many noted observers, among them being Humboldt, Bunsen, Regnault, Lewy, Frankland, and Macagno. The chief objection to its use is that it is not sufficiently delicate, permitting, as it does, a possible error of about 0.0002 of the total volume, where the diminution due to absorption of carbon dioxide is but 0.0003 to 0.0004. A simple calculation will show that error of one-twentieth of a milli-

meter in reading the mercury scale or an error of one-twentieth of a degree in temperature changes the number by nearly its entire value.

(*b*) *Gravimetric.* — De Saussure, whose adventures with his 45-liter glass balloon have already been mentioned, was one of the first to determine the carbon dioxide gravimetrically. He poured out the mixture of barium hydroxide and carbonate, conscientiously washing out the balloon, filtered the whole, washed the barium carbonate and then weighed it. No precautions were taken to avoid contact with the carbon dioxide of the air during the filtration and washing of the barium carbonate, such refinements of accuracy being then deemed unnecessary. Later observers have followed the same lines; but on account of the great difficulty in preventing contact of the caustic solution with the air during the various operations, their results are hardly of sufficient importance to warrant consideration in a brief summary.

(*c*) *Volumetric.* — A number of methods have been proposed, differing from one another in details of apparatus, but all based upon the general idea of absorption of the carbon dioxide in a known amount of standard alkali and titration of the excess above that required for the absorption. Glass vessels of from 2 to 15 liters capacity have been used, in which the air is allowed to stand in contact with the alkaline solution for from two hours to a week. The titration of the excess of alkali may be carried out with sulphuric or oxalic acid, employing various indicators. The most widely known of these methods is that of Pettenkofer, which is discussed more fully below.

Group II. Methods requiring the use of aspirators in order to bring greater quantities of air into contact with the absorbing solutions, used more especially for determining the carbon dioxide in outdoor or "fresh" air.

(*a*) *Direct weighing of the absorbing apparatus.* — This method is based on the assumption that an increase in weight of the absorbing solution is due solely to the absorbed carbon dioxide. There are two sources of error in this unmodified statement. In the first place, the absorbing material may take up water from the air in addition to the carbon dioxide; and second, the previously dried stream of air may remove water from the absorbing solution. This latter source of error may, however, readily be avoided by drying the air again after passing the absorbent and noting the weight of water obtained. On account of its simplicity this method has for a long time been a favorite

one, especially since it affords opportunity for the simultaneous determination of the water vapor of the air.

Brunner[1] used a twice-bent tube about a foot long, the first half being filled with calcium hydroxide to absorb the carbon dioxide, and the other half with asbestos moistened with sulphuric acid to take up the water lost by the lime. Others at different times have used pumice soaked in caustic potash, solid potassium hydroxide, potash or barium hydroxide solution in absorbing bulbs of various shapes and degrees of efficiency.

It would seem that this might be made into a simple and accurate method, but later observers have pointed out its untrustworthiness. Hlasiwitz[2] showed that the amount of carbon dioxide was much too small in proportion to the size of the absorbing vessels (in one case the total surface of the bulbs, etc., which had to be weighed was estimated to amount to 7 square meters), so that accurate weighing was impossible unless a great quantity of air was used. Hlasiwitz called attention also to the fact that the method adopted for drying the air made a decided difference. The Rogers brothers had already shown that sulphuric acid absorbs carbon dioxide. Calcium chloride was condemned by Hlasiwitz after he had shown that silver nitrate was rendered turbid by air which had been passed through a 10-foot tube containing the drying agent. Further, he remarked that potash solution absorbs oxygen as well as carbon dioxide. It was shown later by Reiset that in the case of pumice moistened with potash this was due to the presence of manganous and ferrous salts in the pumice.

(*b*) *Titrimetric.*—This method was used first, in 1857, by von Gilm. Air was drawn through a tube a meter long, bent at one end and drawn out at the other. The tube was inclined and contained barium hydroxide solution as the absorbent. In order to control the completeness of the absorption, flasks of the same solution were placed between the tube and the aspirator. Sixty liters of air were drawn through, the solution filtered, the barium carbonate converted into chloride, ignited, and the chlorine determined by titration with silver nitrate. From the nature of the case only very dilute barium solution could be employed, which rendered complete absorption of the carbon dioxide difficult. The only way to avoid this was to aspirate very slowly, thus increasing the time. Hence all later observers have endeavored

[1] Pogg. Ann., 1832, p. 569.

[2] Wien, Akad. Sitzber., 1856, p. 189.

to bring the air into the closest possible contact with the absorbing solution. This has best been done by Reiset, who by means of a comparatively small apparatus has been able to absorb the carbon dioxide completely when the air is passed at the rate of 100 liters per hour.

To test the completeness of the absorption most observers have used barium hydroxide, noting whether or not it remained clear. The correctness of this procedure depends, of course, on how nearly barium carbonate is insoluble; concerning this opinions vary. Kremers found that 1 liter of water dissolved 83 milligrams of barium carbonate; Fresenius, 71 milligrams; Bineau, 21 milligrams; Schlosing, 18 milligrams. The difficulty of completely absorbing the carbon dioxide from great quantities of air has been shown by Eliot and Storer. They drew 156 liters of air, at a rate of 26–31 liters per hour, through three sets of absorption apparatus, provided with five bulbs each, filled with potassium hydroxide, and found that lime water placed after these remained perfectly clear, but always showed traces of calcium carbonate after standing twelve hours. (It has been stated recently that this action is due to the very gradual oxidation of organic matter in the alkali itself.)

(*c*) *Volumetric.* — This class of methods, in which the volume of carbon dioxide is measured after absorption and subsequent liberation by sulphuric acid, was first proposed by Tissandier in 1875. He used it for the collection of air samples during a balloon ascension. The method was worked out more fully later by Muntz and Aubin, who absorbed the carbon dioxide in glass tubes about a meter long by means of pumice moistened with potash solution. After the aspiration of a definite amount of air, the tube was sealed off and taken to the laboratory, where the gas was set free by sulphuric acid, and measured over mercury with many precautions and the use of a complex apparatus. On the recommendation of Dumas this method was employed by the expedition sent by the French Academy of Sciences to Central and South America, to observe the transit of Venus in 1882. Only simple operations are required from the observer, and the sample can be subsequently analyzed in the laboratory by a competent chemist.

The question of the determination of atmospheric carbon dioxide possesses value beyond that of its mere historical development. It is of very great interest as a critical study, and from that point alone it

would well repay one to make a careful study of the literature. Even a hasty glance over the published memoirs reveals many facts of interest.

In the first place, attention may be directed to the tabulated results of two observers.

| Duration of time. | Observers. | Number observations. | Carbon dioxide in 10,000. |
|---|---|---|---|
| 1828–1830 | 1 (Saussure) | 201 | 4.1 |
| 1830–1856 | 6 | 322 | 3.6 |
| 1856–1885 | 22 | Over 4,000 | 3.1 |

OBSERVATIONS OF TH. SAUSSURE OVER A PERIOD COVERING TWENTY-TWO YEARS.

| Time. | Number observations. | Carbon dioxide in 10,000. |
|---|---|---|
| 1809–1815 | 6 | 6.0 |
| 1816–1828 | ? | 4.9 |
| 1827–1830 | 227 | 4.1 |
| 1827 | 26 | 5.1 |
| 1828 | 64 | 4.4 |
| 1829 | 135 | 4.0 |
| 1830 | 2 | 3.7 |

Schultze also, from 1863 to 1871 (with one break of four years), made daily determinations of carbon dioxide in the air of Rostock.

| Time. | Number observations. | Carbon dioxide in 10,000. |
|---|---|---|
| 1863–1864 | 431 | 3.64 |
| 1868–1871 | 1,034 | 2.92 |

These results are typical of many, and it may be said in general that the later results of all observers are lower than their earlier ones. It is a fair assumption that the methods have been gradually improved, and that the later results are more nearly correct. The cause of the

great difficulty lies in the nature of the task. It is necessary to estimate accurately a portion which makes up only three ten-thousandths of the body examined. An error which amounts to only one-millionth of the total changes the value by nearly 1 per cent. Hence a study of the sources of error is most important.

Among forty of the early workers (before 1887), only two made experiments to determine the *total of all sources of error.* In both cases (von Gilm, 1875, and Muntz and Aubin, 1882) the observers added to air free from carbon dioxide a known amount of the gas and determined it by the method used. Von Gilm used 60 liters of air in which he had found as the average of nineteen determinations 0.0490 gram of carbon dioxide (4.15 parts). In the control experiment, to air free from carbon dioxide he added 0.0449 gram of carbon dioxide and found 0.04475 gram. He was therefore satisfied that his method possessed a high degree of accuracy. It is today, however, known beyond a doubt that 60 liters of "fresh air" contain *0.0354* gram of carbon dioxide, and according to this his results were *38.3 per cent. too high.* He must of necessity, then, have made an error in his gas mixture equal to the error in the determination, and opposite in direction. It so happened that von Gilm's results agreed almost perfectly with those of Saussure (4.1), which were then generally considered correct. These two facts alone have greatly hindered the development of the truth concerning the amount of carbon dioxide in atmospheric air. Thus Pettenkofer, introducing his now well-known method in 1858, tested it by parallel determinations with the method of von Gilm, and was satisfied with the accuracy of his procedure. Following this came the nearly universal and widespread use of the Pettenkofer method.

Various observers have determined the error due to the separate operations in the procedure. Thus the influence of the various errors in the weighing; the delicacy of the different indicators used in titrating; the completeness of the absorption, etc., have all been critically studied. Most observers, however, have been content to make parallel experiments with the same method, which would tell of occasional errors but not of some constant error of the method.

For example, one of the earliest people to make quantitative determinations of carbon dioxide was Alexander von Humboldt. After describing the apparatus that he used, he goes on to speak of the necessity for knowing the possible sources of error, and states that

as a result of many experiments "on the same air in different tubes" he is assured that his results cannot differ from the true amount by more than 0.003. From our present knowledge it is apparent that the possible error, or rather the probable error in this case, was about ten times the amount of the quantity to be determined.

It might almost be said that the fact that most of the early observers neglected certain fundamental principles of quantitative analysis is the reason why our knowledge of the carbonic acid content of the air is so slight in comparison with the time and labor that have been spent upon it.

The determination of carbon dioxide in outside or "fresh air" is by no means, however, the only case in which the determination is of value; perhaps it is not even the most important. The determination of carbon dioxide in the air of enclosed spaces, in dwelling rooms and halls, is of great value as a means of determining the efficiency of systems of ventilation; lately as a method for showing the overcrowding of workrooms through the vitiation of the air, it has become of legal importance.

For these purposes the aspiration of large quantities of air is impracticable; furthermore, since the proportion of carbon dioxide in confined air is almost invariably higher than in outside air, such methods are unnecessary. In such cases it is customary to collect a small sample of air, from 2 to 10 liters, and to examine it by some modification of the so-called Pettenkofer method. Since this method is so generally used, a few words concerning it may not be out of place here.

The fundamental principle of what is now known as the Pettenkofer method is extremely simple. A definite sample of air is collected, usually in a glass bottle, the carbon dioxide is absorbed by lime water or by barium hydroxide, and the excess of alkali is determined by titration with standard acid, using a suitable indicator. The idea was not original with Pettenkofer. Dalton and his pupils, Hadfield and Watson, had already described a method in which they collected air in a glass globe, absorbed the carbon dioxide in lime water, filtered and washed the precipitated chalk, and titrated the excess of lime water with dilute sulphuric acid.

These investigations were either not generally known or had been forgotten when Pettenkofer published his method in 1858; but it is clear that the principle of his method had been anticipated.

Most text-books describe as Pettenkofer's a method which was not

his and which lacks many of the safeguards that he adopted. In the method as first described, Pettenkofer used a bottle closed by rubber, and titrated the solution directly through a small tube, letting down a piece of turmeric paper from time to time through another tube. He drove the air into the bottle by a bent tube, which was so arranged that it could be pointed in any direction in which it was desired to collect the sample; but as the tube was only 6 inches long, it didn't make much difference about changing the direction. Angus Smith used a confectioner's jar, into which he could put his hand to clean it.

This method possesses many distinct advantages. It demands but little in the way of apparatus, and requires but little time for its execution; it tells the condition of the air at a given moment; it is sufficiently simple to avoid many of the errors on the part of the observers due to the more difficult manipulation of other methods. Some such method is much to be desired, on account of the uncertainty of complete absorption in the aspiration methods.

On account of this very simplicity of apparatus and procedure the method, however, is open to several serious sources of error. Contact of the breath of the operator or of the air of the laboratory, often rich in carbon dioxide, with the absorbing solution; the action of the alkaline solutions upon the glass of the bottles used for collection; incomplete removal of barium carbonate before titrating for the excess of alkali — all of these vitiate the accuracy of the results. It has been claimed that the use of rubber stoppers in closing the bottle leads to incorrect results, since rubber absorbs carbon dioxide and also gives off the same substance through oxidation, this latter action taking place with especial ease in the presence of alkaline solutions.

It is possible, however, to avoid these sources of error by suitable arrangements, although thereby increasing very considerably the delicacy of manipulation necessary and the complexity of the apparatus. This has been done by several observers, and with notable success by Letts and Blake.[1] A brief outline of the precautions which they found it necessary to adopt will best illustrate this point.

The receivers used for the collection of the samples were 5-liter flasks heavily coated on the inside with paraffin wax. The samples were collected by an air pump through a rubber tube 15 feet long, in order that the sample should not be drawn from within the area of contamination. The stock bottle for the barium hydroxide and the

[1] Proc. Royal Dublin Soc., 9, 107 (1900).

pipette used to measure the charge of alkali were both coated with paraffin. The charge was run into the bottle in such a way as to avoid all contact with the air, and the bottle rolled on its side at intervals for two or three hours in order to absorb the carbon dioxide. After the absorption was complete, the solution was drawn off by suction into a receiver exhausted of air, and the large flask washed out several times in the same way with water free from carbon dioxide. The titration was carried out in the exhausted receiver, using dilute acid in narrow burettes of special design. With careful work it was found possible to secure results agreeing within two or three hundredths of a part in ten thousand on outdoor air. The results on known mixtures which contained carbon dioxide in about the proportion in which it exists in fresh air also showed satisfactory agreement.

As to the proportion of atmospheric carbon dioxide and its variations, comparatively few deductions may be drawn from the mass of material which has been gathered. A not inconsiderable portion of the numerous researches have served but for this: that the earlier errors were removed. Furthermore, it is only by viewing the matter from a point sufficiently far withdrawn, both in time and prejudice, that a satisfactory estimate of the subject may be made. Conclusions drawn from individual work are dangerous. Levy, for instance, in 1847, found that the air over the ocean contained more carbon dioxide than the air over the land. Thorpe, in 1866, found that the condition was exactly the opposite.

The conditions attending the collection of samples vary so that reliance can be placed only on the average of many analyses. During Reiset's examination of the air near Dieppe, he says: "The presence of a flock of 300 sheep in the neighborhood of the apparatus during a fine, calm day was revealed by a notable augmentation in the proportion of the carbonic anhydride; 3.178 volumes were obtained in 10,000. (The average for Dieppe was found to be 2.963 volumes.)

Differences due to strictly local causes may be very noticeable. Russell, as the result of a study lasting for two and one-half years, found the average amount of carbon dioxide in the air of London, exclusive of the days on which there were fogs, to be four parts per 10,000 as against three in the country. The two lowest results, three and three-tenths parts, were found in two successive years on the "Bank Holiday," when many of the clerks were out of the city for the day.

The chief sources of the atmospheric carbon dioxide are: combustion, putrefaction and decay, fermentation, all of which are more or less temporary; volcanic and subterranean fires, which are the most important permanent sources. Sources of absorption are the weathering of rocks, change of silicates to carbonates, the formation of corals. As regulating agencies we have the reciprocal action of plants and animals and the more or less automatic action of the oceans, which absorb carbon dioxide to form bicarbonates and give it off again with increase of temperature.

It may be stated as a general conclusion that, so far as our present knowledge goes, the average amount of carbon dioxide in fresh air is very close to *three parts in 10,000.* From this average amount there is, however, a constant variation, due to causes both local and general.

CONTRIBUTIONS FROM THE LABORATORY OF SANITARY CHEMISTRY.

VII.

# *NOTES ON OSCILLARIA PROLIFICA (Greville).*

BY ISABEL F. HYAMS AND ELLEN H. RICHARDS.

THIRD PAPER: COLORING MATTERS.

THE composition and character of the cell contents of this plant possess renewed interest in the fact, apparently substantiated, that its protoplasm is rendered inert by copper sulphate, and therefore it belongs to the group of Cyanophycæ which may be removed from water supplies.[1]

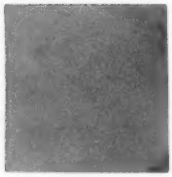
As has been shown in this journal (XIV, p. 302, and XV, p. 308), the optimistic temperature of its growth is 64° to 66°, and each spring, for fifteen years, Jamaica Pond has become more or less opaque with its threads within a few days after the water becomes warm enough, the maximum amount occurring in from two to three weeks, culminating, in every normal season, in one or two days, never more, when the plant comes to the surface after a day of rapid growth, buoyed up by the gas bubbles formed during the night. This never happens except the air temperature of 80° and over is accompanied by a bright sun and quiet water. When this proliferation, as it were, has taken place, the long fibers break up as shown in this journal (XIV, p. 308).

From 1895 until this season, filaments of various lengths could be found in deep water and on the slimy stones at 1 to 2 feet in depth at all seasons; and in a cool August a second growth took place, not as vigorous nor of the purple or even bright green color, but yet sufficient to give a decided scum of dirty greenish white.

In September the round, spore-like bodies are formed, some years in considerable abundance, but always few in comparison with the amount of the plant in the water. In certain seasons, under favorable

[1] Bulletin 64, Bureau of Plant Industry, United States Department of Agriculture. Reports of Massachusetts State Board of Health, 1903, 1904.

PLATE I.



No. 3.

No. 4.

No. 2.

No. 5.

No. 1.

No. 6.

ILLUSTRATION OF COLORS OBTAINED FROM OCILLARIA PROLIFICA.

Mounted at the Manhattan Trade School for Girls.

conditions, they appear to start growing new filaments in October, and in that case there may be less abundant growth the next spring.

In 1902 the conditions were unfavorable (this journal, XV, p. 315), but in 1903 an unusually luxuriant growth occurred, showing that the presence of the geese and swans had not changed the character of the food supply. It was estimated that at least 100 barrels of the solid scum might have been obtained in these two days, yielding nearly a ton of the dried plant in a nearly pure condition.

The copper sulphate was applied September 23, 1903, not at the time of greatest growth of the plant, May 12 and 20, but at the "spore" forming time; and it would seem as if the young plants, as well as the broken filaments, absorbed and were killed by the solution, since on October 5, 6, and 7, a considerable film of the algæ came to the surface bleached nearly white, but containing copper in a considerable quantity.

The filaments were narrow, like young ones, although they may have shrunken; yet this siliceous skeleton holds its shape through all kinds of chemical treatment except that with strong potassium hydrate.

From the time of the throwing up of this film only a few threads have been found in the water. They were not found on the bottom, as usual in the winter, and only a few grew in April and May, 1904, and none have been found since May 23; many samples of 2 liters each, taken at frequent intervals, have shown none at all.

As was stated in this journal (XIV, 1901, p. 310), in early spring the first filaments are yellow to dirty greenish white; then when growing more freely, are blue green; and when luxuriant, or whenever the growth is rapid, a deep rich chocolate with a reddish tint (Plate I, No. 1); whereas later in the season, when there is little growth, the color is a bright blue green (No. 4).

When the plant is allowed to dry exposed to air and light in a thin layer, as on the rocks of the shore or on paper or cloth, it takes on a beautiful violet tint (No. 3) after a few days. No means yet tried has availed to produce this color artificially, either in the plant or from any extract. The tint varies in purity and richness with the quantity of the red coloring matter present in the alga at the time of collection, and therefore bears some, as yet undetermined, relation to the latter.

If the drained but moist mass is allowed to stand in glycerine in a cool place for a month or more, a rich red violet (No. 2) appears all

through the plant filaments, probably in the granules, enclosed in or adhering to the *septa* "stores of reserve material."[1] Only a small portion of the color goes into solution in the glycerine. No other solvent has been found which will extract this color unchanged. This solution is red violet (Nos. 2 and 3) by transmitted light, and orange red (No. 1) by reflected light. Aluminum hydrate forms a brilliant lake, but neither silk nor wool takes up the color.

Treatment of the fresh, moist or quickly dried — unfermented — substance by gasoline or petroleum ether yields the usual phyllocyanin and phylloxanthin (phycocyanin and phycoxanthin of some authors[2]), and what appears to be an unusual amount of a dark green oil, probably the chloroglobine of de M. Tsvett.[3] Nadson[4] claims that the phycocyanin of the *oscillarias* is most nearly allied to phycoerythrin, and belongs to the group of hydrochromes.

If the substance treated is fresh and moist, these forms of green coloring matter carry with them in suspension, if not in solution, in the gasoline a beautiful red color, which on long standing in a separatory funnel protected from the light deposits red crystalline forms, elongated octahedrons. The color (No. 5) is left in an amorphous form if the solution is evaporated and then taken up with fresh gasoline. The red color coagulates, as it were, and becomes insoluble. Further treatment by boiling alcohol or chloroform yields an orange-red solution (No. 6) (also a dye for silk and wool), which under certain conditions deposits brilliant iridescent plates of the red color.

The addition of sodium acetate to the alcoholic solution leaves on evaporation red crystals which dye silk and wool (No. 5). This may be Chodat's myxoporhyrin,[5] which he considers as probably identical with Sorby's pink phycocyanin. Professor Chodat has studied the rare *oscillaria rubescens* which appears occasionally (in warm seasons) on the surface of Lake Morat, in Switzerland, in such quantity as to impart a pink color to the water. Harvey[6] claims that the microscopic alga (trichodesmium erythroeum) which occasionally flourishes in such

[1] F. A. Marx, Jour. Royal Micro. Soc., 1893.

[2] M. N. Montverde, Acta Hort. Petropol, 1890, pp. 123–178.

[3] Compt. Rendus, CXXXIX, 1899, pp. 607–610.

[4] Scripta Botanica, IV, 1892. Bot. Cent. Vt., LIII, p. 315; LV, p. 72.

[5] Jour. de Bot. (Morot), 1896, pp. 341–349, 405–409. Jour. Royal Micro. Soc., 1897.

[6] William H. Harvey, Contributions to a History of the Marine Algæ of North America. Smithsonian Contributions to Knowledge.

quantities in the Arabian Gulf as to redden the sea for many miles, and which probably gave it its name, is allied to the *oscillariæ*, and that it has similar motive power.

Lankester has studied bacterio-purpurin from violet-colored bacteria which exhibit great avidity for light. The pigment in this case is said to occur exclusively within the cells in the part of the contents immediately adjoining the walls.

The relation of color to plant metabolism is receiving attention in various quarters. Schunck for many years worked on the components of chlorophyll and isolated from it a red-colored substance having many of the characteristics of hæmoglobin.

It is the red color which has most strongly fixed our attention, for two reasons: red is rarely found among the algæ, and there seems to be good reason to suppose that in this substance there lies at least one of the keys to the process of plant metabolism, as we shall now endeavor to show.

The chlorophyll of the algæ appears to be identical with that of other green plants, although the relative proportions of erythrophyll,[1] xanthophyll, cyanophyll vary more widely. These early names mean groups rather than definite substances, and only in recent years have the studies of the Schuncks and Marchlewski shown that more definite substances may be obtained. They say[2] that a product deserves the name of chlorophyll only if it yields, under the influence of acids, phylloxanthin and phyllocyanin.

The same authors[3] seem to have demonstrated that from chlorophyll may be derived a color stuff — phyllophyrin — which in composition and chemical characters stands very close to hæmatoporphyrin, an iron-free color stuff found in the blood of man and animals, $C_{16}H_{18}N_2O$. The spectra of these two substances also are identical, thus bringing into close relation the portion of living matter common to both animal and vegetable life.

While it has long been recognized that chlorophyll is of high biological significance, because upon it or upon one of its components

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[1] Phycoerythrin, Kützing, Algæ. Leipsic, 1843.

[2] Jour. of Chem. Soc., September, 1900.

[3] Dr. Schunck, A Résumé of the Researches into the Nature and Constitution of Chlorophyll since 1889, Ann. Bot., VI, 1892, pp. 231–244. C. A. Schunck, Jour. Micro. Soc., 1893–1899; Pro. Royal Soc., LXV, 1899, pp. 177–186; and Ed. Schunck, Annalen, 1895, pp. 284, 81, 107. Leo Marchlewski, Jour. Pro. Chem., 1898, II, pp. 57–330, 334; Jour. Pro. Chem., 1899, pp. 91–96. Leo Marchlewski and C. A. Schunck, Jour. Chem. Soc., September, 1900.

depends the metabolism of the plant — its carbon assimilation — these late investigations renew the somewhat waning interest in this group of substances. The authors venture to suggest the theory that this red substance, which they have tentatively named rubescin (from *oscillaria rubescens*), is an important factor, if not the chief one, in the vigorous growth of plant life. It may be stated as follows: —

Good red blood and a portion of red in the chlorophyll of green plants wherever found seem to indicate robust life.

Every observer will recognize the very marked instance given by the quick and vigorous growth of young shoots of oak, maple, and several other trees and shrubs growing up in a sunny clearing in the forest, where the food is abundant. These quickly growing ends are frequently, if not generally, red. The richness of the June growth in comparison with the delicate, more transparent yellow of May is apparently also due to this red substance.

The association of the red color with vigor of growth seems to be well worth studying further. To the authors' knowledge this has not been suggested, and indeed would have had no reason to be before the discovery of the close relation to the hæmoglobin of animal blood.

An admirable summary of facts and theories is given by Miss F. Grace Smith[1] in a study of the distribution of red color in the stems, leaves, and other vegetative parts of plants. Her conclusions that the joints of stems, the upper surface of leaves, exposed parts of plants in dry, sunny places, are generally red, admit of our theory that the presence of visible red indicates the *rapidity* of growth, the always present nitrogenous substance being naturally more abundant and therefore noticeable when the process of assimilation is at its best. The same thing is very marked in the purple or copper beech, which goes through several stages of coloration in the course of the season. First a delicate yellow brown, then red and deep purple, and finally a bluish green, except in the most exposed situation, where the leaves retain the red color until quite late. This is the only case which seems to us to countenance the theory that the red is a protective device, for trees not exposed to the strongest sunlight lose their color quite early in the season.

From this point of view it is instructive to compare the analyses of young and of fully grown specimens of *oscillaria*.

[1] On the distribution of red color in vegetative parts in the New England Flora. Bot. Gazette, XXXII, November, 1901, p. 332.

| | I. Very pure young threads. | II. Fully grown (see Figure 1). |
|---|---|---|
| Ash | 4.50 | 6.40 |
| $SiO_2$ | 1.46 | 2.90 |
| N | 9.00 | 7.90 |
| $P_2O_5$ | 0.89 | 0.54 |
| S, undetermined | . . . | . . . |
| $Fe_2O_3$, $Al_2O_3$ | 0.40 | 0.50 |

Herr J. Tammes[1] concludes that the pigment of the plastids from green leaves and from blue-green algæ, etc., agrees in all its chemical and physical properties with the carotin of the carrot, which he has studied. He further states that this substance is an invariable accompaniment of chlorophyll in the plastids of all parts of plants which are capable of carbon dioxide assimilation.

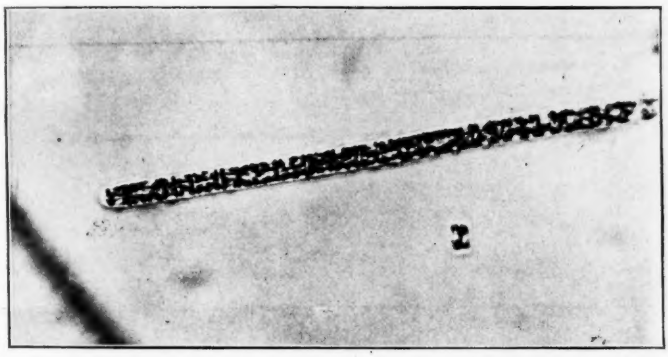

PLATE II. — FILAMENT OF OSCILLARIA PROLIFICA, MAGNIFIED (?).

During the periods of rapid growth and excess of red color in the *oscillaria* the water of Jamaica Pond loses its free carbon dioxide completely and becomes alkaline.

The percentage composition of the red color has not yet been determined with certainty, but it contains nitrogen and sulphur and

[1] Jour. Royal Micro. Soc., 1900, p. 599; and Flora, LXXXVII, 1900, pp. 205, 247.

appears to be of an albuminous nature. It apparently yields skatol, or a very closely related body — a substance which to the authors' knowledge had not been found from purely vegetable decomposition previous to their identification of it in 1897. The colors given by two of its derivatives are shown in No. 2 and No. 5. The discussion of this and another most interesting substance, a saponin-like constituent, is reserved for a future paper.

Plate II shows a late photograph taken by Mr. Louis S. Brown, of the Massachusetts General Hospital.

CONTRIBUTIONS FROM THE LABORATORY OF SANITARY CHEMISTRY.

VIII.

# *PERMANENT STANDARDS IN WATER ANALYSIS.*

BY LILY MILLER KENDALL AND ELLEN H. RICHARDS.

EVERY chemist has noted with regret the hours that are consumed in preparing the various color standards for comparison, now so universally used for the determination of the small amounts of ammonia, nitrites, nitrates, and other substances occurring in water.

Nearly every analyst has tried to minimize this time expended by some mineral solutions of his own or others' devising, which will keep indefinitely and be always ready.

There are two insurmountable obstacles to perfect success; first, that such pure or mixed solutions, frequently strongly acid, have a clearness and brilliancy of tone which the complex sample to be matched never possesses; and second, that the color produced in the solution to be tested depends upon a variety of conditions: temperature, quantity of reagent added, manner of making reagent, variable quantity of accompanying substances, time elapsing after preparation before comparison of color, and a score or two more, practically impossible to control perfectly. The determination of ammonia by the Nessler reagent is a familiar example.

These difficulties may be removed to a greater or less extent by careful preparation of the standards from solutions as nearly as practicable of the same order of variability.

Hence it is that permanent standards, made up to match a given set of conditions, cannot be relied on under *all other circumstances.* Nevertheless they have their uses; and for field work, where comparison within certain limits only is to be exacted, approximately permanent standards for all the common tests serve an admirable purpose.

In preparing a portable field apparatus for the Louisiana Purchase Exposition two or three combinations were devised which may prove

of interest and may suggest other experiments along the same line. The Griess test for nitrites is one of the most valuable for field work, but in the conditions under which tests must be made — lack of pure rinsing water, dusty atmosphere and hasty work — the very unstable nitrite standard is a source of anxiety, and therefore a set of permanent standards is much to be desired. Such a set lessens also the quantity of troublesome reagents to be carried.

A very satisfactory tint of color, which remained permanent for two months in the winter in the even temperature of the laboratory, was given by a solution found among the set of indicators marked "Corallin, Malachite Green." This solution unfortunately was of unknown origin, and attempts to duplicate it exactly have not been wholly successful. The results are here given simply as suggestions for further work. The substance desired is very possibly "corallinephthalin or pseudo-rosolic acid, the chief constituent of commercial aurine." Organic Coloring Matters, Schutze & Julian, translated by Green, 2d edition, p. 198.

A sample of Kaulbaum's aurin found in stock, when made up in about the proportion of 1.5 milligrams per liter matched fairly well the 10 c.c. standard nitrite. A sample of Kaulbaum's rosolic acid of the same strength, to which was added .008 milligram in aqueous solution of Kaulbaum's "malachite green," gave a color very closely approximating to the 20 standard. There are several commercial substances listed under the name malachite green; this seems to be "B," giving a blue-green aqueous solution, which is discharged by excess of potassium hydrate; therefore since aurin or rosolic acid must be in decidedly alkaline as well as alcoholic solution, a somewhat delicate balance of conditions must be formed. The solution once obtained, however, it seems to dilute in proportion and give an excellent match of tint. The blue in the aurin seems to fade out unless the solution is kept very strongly alkaline, leaving a yellower tint than desirable. This is the case with the standards prepared from the usual reagents. If, as now appears probable, the strong solutions carefully protected will keep, and may be diluted as needed, the test may be of some value.

Standards for the Grandval and Lajoux nitrate test were made from the neutral potassium chromate used for indicator in the chlorine test. For the deeper colors and ammonia, a solution made after Tidy's formula was found to be practicable for dilution to the de-

sired tints. $K_2Cr_2O_7$, 0.25 grams; $CoSO_4$ $H_2O$, 9.05 grams per liter. This solution avoids the strong acidity so unpleasant in portable cases.

In the two long trips[1] made with the portable apparatus described in this journal,[2] it was found that the form of the case, convenient in

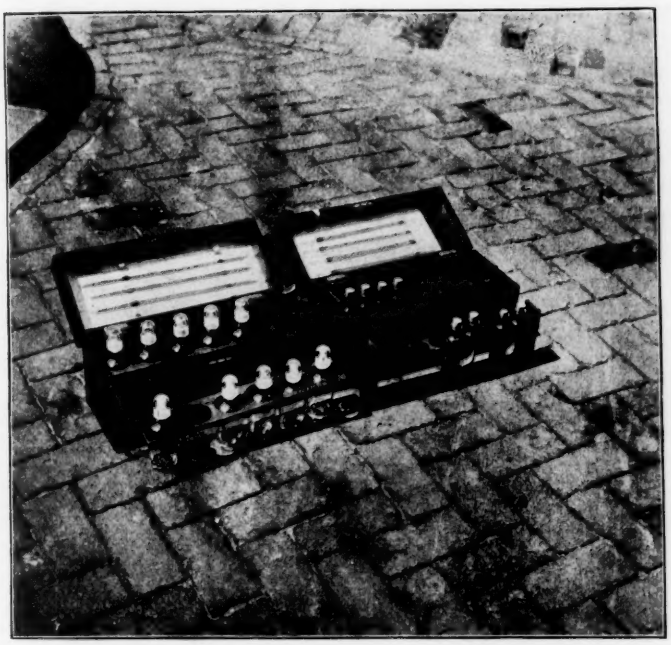

FIG. 1.— PORTABLE CASE FOR FIELD WORK IN WATER ANALYSIS.
Length, 16 inches; depth, 6½ inches; height of each box, 7½ inches.
Designed by Mrs. Kendall.

many respects, was most unsatisfactory to transport in sleeping cars; for, unless watched over like a bag of gold, the porter would inevitably lay it on its side, to the imminent danger of loosened stoppers and

[1] The Water Supplies of Southeastern Alaska. Notes on the Water Supplies in the Black Hills of South Dakota and Vicinity. TECHNOLOGY QUARTERLY, XVI, No. 4, December, 1903.

Notes on the Potable Waters of Mexico. Transactions American Institute of Mining Engineers, XXXII, 1902, p. 335.

[2] A Portable Outfit for Water Analysis. A. G. Woodman, TECHNOLOGY QUARTERLY, XIV, No. 4, December, 1901.

promiscuous mixture of reagents. The same difficulty occurred when driving across country in a buggy. This close, personal care becomes irksome in the course of weeks. The form shown in the figure is designed to obviate these difficulties.

Two boxes fitted up after the manner of instrument boxes are to be strapped together when carried by hand, but when separated may be slipped under the berth or wagon seat and kept right side up.

The removable racks, with the permanent standards and free bottles for comparison, will be found to facilitate observation. The bottles for reagents, with double ground glass stopper joints, may prove too frail for rough carriage; but fastened with the yoke, as shown in the left hand of the illustration, they should stand well.

The padded cover furnishes safe resting place for the pipettes, and the narrow space behind the racks allows for the carriage of the various additions which each chemist would choose for himself. The English Thresh portable case with solid reagents is still more compact but nearly as heavy, and does not permit of all the tests used in this country. Many of the most useful "soloids" can be put up to order in this country and added to the suggested outfit.

CONTRIBUTIONS FROM THE LABORATORY OF SANITARY CHEMISTRY.

## IX.

## *NOTES ON THE "HARDNESS" OF WATERS.*

BY CHARLES R. WALKER.

IT is well recognized that the simple and convenient test for "hardness" in waters, indicating the amount of earthy or soap-curdling substances present, by a standard soap solution, gives good results only within certain limits, and with waters not over 100 parts per million.

Engineers are, however, often confronted with waters ten times as hard. It was in the course of some experiments on such hard waters, and with the object of classifying them, that the following experiments were undertaken at the suggestion of Mrs. E. H. Richards.

Two methods presented themselves: —

First. To use a stronger soap solution.

Second. To use less volume of water than the usual 50 c.c.

In the first experiments a soap solution ten times the usual strength was standardized with a solution of calcium chloride, also ten times the usual strength, *i. e.*, containing 1 gram of pure Iceland spar in 500 c.c. of distilled water; but it was found to be so difficult to determine the end point, owing to the thick white curd or floating layer of insoluble calcium soap, that it was finally decided to standardize and also to make the tests by using 5 c.c. of the water to be tested diluted to 50 c.c. with distilled water.

The titration was carried out from a 10 c.c. pipette, graduated to $\frac{1}{10}$ c.c., and capable of being read to $\frac{1}{100}$ c.c., fitted up as a burette.

Five cubic centimeters of the Iceland-spar solution, made in the usual way, but ten times the usual strength, required 1.425 c.c. of soap solution.

This worked fairly well, but it was found that with very hard waters there was still difficulty in determining the end point, owing to the curd.

Coloring the solution with phenol phthalein was found of no advantage.

Finally an attempt was made to determine the end point by sound, and titrations were made with the burette covered so as to prevent possible bias of judgment. It was found to be quite easy to titrate to within $\frac{5}{100}$ of a cubic centimeter. This was done several times on known waters at intervals of several days and under such conditions as to prevent the reading being influenced in any way.

By this method it was possible to titrate 50 c.c. of a solution of calcium chloride ten times the usual strength with a soap solution also ten times the customary strength, the end point being determined as follows: —

First, by sound. The harsh sound as of solid and liquid is suddenly deadened, as if oiled, as the end point is reached.

Second. It was noticed that until the "earthy" salts were all precipitated by the soap, the larger bubbles broke almost instantly and without iridescence, but when the soap was in *slight* excess, or the end point was reached, the larger bubbles lasted from one to two minutes and showed marked iridescence.

Thus there were two indicators, calling into use both the ear and the eye. Check determinations could be made in this manner with surprising accuracy, and the range of waters capable of being determined by the soap method was considerably increased.

Experiments were also made to determine the effect of diminished volume, *i. e.*, using less volume than the customary 50 c.c., with the result that it was found that by the use of the "sound" method uniform results could be obtained irrespective of the volume taken, and also that within reasonable limits the size of the bottle did not make appreciable difference in the determinations, provided round bottles were used, since the surface of the liquid decreased in proportion to the decrease in volume of the liquid used.

It was found that the practice of diluting a water with distilled water was distinctly harmful, and that more uniform results were obtained *not* by diluting, but by taking the hard water direct and titrating with the strong soap solution, using the sound as indicating the end of the reaction, and paying no attention to the heavy curd formed, or to other appearances than the iridescence and permanence of the larger bubbles.

By this method the number of cubic centimeters of soap solution

required by 5 c.c. of the water, titrated direct, without dilution, multiplied by ten, gave very closely the number of cubic centimeters of soap solution required by 50 c.c. of the water when titrated direct.

That this is not the case when the usual method is followed of taking a smaller quantity of the hard water and diluting it to 50 c.c. with distilled water is well known, and it is this discrepancy that the method of using stronger solutions and titrating by sound seems to obviate.

## *THE HYDROLYTIC ENZYME CONTAINED IN CASTOR-OIL SEEDS.*

By W. H. WALKER and L. M. BOURNE.

Although wonderful progress has been made during the last few decades in every line of applied chemistry, it is but very recently that many reactions long known to occur of themselves in nature have been made of technical value. An example of development along these lines is found in the application of the enzyme occurring in the seeds of the castor bean (*Ricinus communis*) to the commercial hydrolysis of fats and oils. The process may be represented by the reaction: —

$$\underset{\substack{\text{Stearin}\\\text{(A neutral fat)}}}{3CH_2OCOC_{17}H_{35}} + \underset{\text{Water}}{3H_2O} = \underset{\text{Glycerine}}{C_3H_8O_3} + \underset{\text{Stearic Acid}}{3C_{17}H_{35}COOH}$$

Present methods for the manufacture of glycerine and the fatty acids are based upon this same reaction, but it is generally brought about by the aid of heat and pressure, with or without the presence of small quantities of a mineral acid.

As early as 1876 Schützenberger pointed out the existence in the seeds of certain plants of a ferment which had the power to thus hydrolyse fats. He gave, however, a very inadequate account of his work, and apparently little notice was taken of it. In 1890 Green[1] and Sigmund,[2] working independently, observed that when certain oil-containing seeds were rubbed up to a paste with water and allowed to stand an acid reaction developed. Later the presence of free fatty acids was detected, and the authors each concluded that there was present a ferment or enzyme which possessed the ability of splitting or hydrolysing the oil.

Nothing further was done in this matter until 1902, when Connstein,[3] Hoyer, and Wartenberg published the results of their work on the castor-

[1] Proc. Royal Soc., **48**, 370.

[2] Monatsh. f. Chem., **11**, 272.

[3] Ber. Chem. Soc., **35**, 3988.

oil seed enzyme and proposed its utilization as a substitute for the heat and pressure at present used for the commercial hydrolysis of fats and oils. According to these investigators the process may be successfully carried on as follows: 50 grams fat, 5 grams of the pulverized seeds, and 10 grams of N/10 sulphuric acid are ground together until an emulsion is formed, and then allowed to stand for twenty-four hours. At the end of this period the mixture is heated and somewhat diluted with water or weak acid, when it separates into three layers: the free fatty acids at the top, then the water containing the glycerine, and, lastly, the seed residue.

Such a process taking place without the application of mechanical energy or any considerable amount of heat and without injurious decomposition products is surely an attractive one, and when the simplicity of the necessary apparatus is taken into account it seems well worth further study. As no data on the technical application of this process were then available, the following experimental work was carried out with a view to determining some of the difficulties that were to be encountered in its development: —

From a large manufacturer of castor oil we were supplied with samples of the seeds of the common castor-oil plant and of the residue from which all the oil had been expressed. This press cake has little commercial value, and, unless the process used to extract the oil had killed the enzyme, would furnish a cheap source of this active agent.

A number of the experiments outlined by Connstein and his coworkers with the fresh seeds were repeated, and, in general, analogous results obtained. Our seeds, however, did not seem to be so rich in the enzyme as those that were used by these investigators, as in most cases a larger percentage of the seeds had to be used in order to get equivalent results. From the press cake as received from the factory no results whatever could be obtained. Laboratory experiments subsequently proved that the temperature used in the oil presses was considerably above that at which the enzyme ceases to act.

Seeds pressed cold did not appreciably lose in enzymic power, but by this method so much of the oil is retained in the press cake that for commercial use it would not be satisfactory. It seems evident, therefore, that press cake as now obtained in the open market is not available for the hydrolysis of fats.

The other common method for the separation of vegetable oils is by extraction with a volatile solvent. To determine the effect of this treat-

ment seeds were freed from their hulls and extracted, carbon disulphide, ether, and chloroform being used as solvents. Hydrolysis experiments on the extracted residues gave the following results:—

| Ratio of fat to residue. | Solvent used in extraction. | Time of hydrolysis in hours. | Percentage hydrolysis. |
|---|---|---|---|
| 10:1 | Carbon disulphide . . . . | 24 | 96.5 |
| 10:1 | Carbon disulphide . . . . | 48 | 97.9 |
| 10:1 | Ether . . . . . | 12 | 91.5 |
| 10:1 | Ether . . . . . | 24 | 94.7 |
| 10:1 | Chloroform . . . . . | 12 | 91.5 |
| 10:1 | Chloroform . . . . . | 24 | 98.9 |

These residues were white, fluffy powders, odorless and tasteless, and gave a marked reaction for enzymes when tested with an alcoholic solution of gum guiacum and hydrogen peroxide. The enzymic power per unit weight was much higher than in the fresh seeds, but not what could be expected if the oil had been simply removed. Since the fresh hulled seeds contain from 50 to 60 per cent. of oil the extracted seeds should be somewhat more than twice as active.

As we were unable to ascertain the age of the seeds under investigation, or obtain seeds which we knew to be perfectly fresh, our study of the influence of time on the enzyme contained in these was not very satisfactory. But neither the seeds as received by us or after the hulls had been removed lost appreciably in enzymic activity during the two months devoted to the work. After extraction, however, the residues, when allowed to stand in the air, rapidly lost their activity; on the other hand, if preserved in an air-tight bottle this decrease was but small.

It is apparent from our experiments that the presence of oxygen hastens the deterioration of the enzyme, and that this may be an additional explanation for the inactivity of the press cake. This oil-free residue was more efficient as an emulsifying agent for the fat than were the fresh seeds.

Although practically all the solvents hitherto suggested for separating enzymes from the substances in which they occur were made the basis of experiment, and in addition, many others, we failed to obtain a

satisfactory solution of the active principle. Not only is no enzyme extracted by salt solutions, glycerine, etc., but the seeds or seed residues thus treated lose their activity. Even a washing with water is sufficient to decrease their enzymic power 50 or 60 per cent. Apparently the oil of the seed is necessary to protect the enzyme from both the air and from moisture.

We had hoped to obtain a concentrated solution of the fat-splitting enzyme similar to the extract of lipase, as prepared from the pancreas of animals, or hypase, the hydrolytic enzyme of the liver, and to use this as an aid to animal digestion. Green, in his original paper, proved that this castor-oil-seed enzyme flourishes in the absence of free acid, while Connstein's experiments showed it to grow only in an acid medium. As the content of the digestive tract below the stomach is neutral, or slightly alkaline, it was important in this connection to determine whether the enzyme could be induced to act under these conditions. Emulsions prepared as already described were made neutral, slightly alkaline, and slightly acid, and allowed to stand at about the temperature of the body for some days. In every case the neutral and alkaline preparation remained without action; those slightly acid slowly commenced to hydrolyse. The speed of hydrolysis increased for a time and reached a maximum after the third or fourth day. As a therapeutic agent, therefore, this enzyme does not promise much unless its properties could be utilized in the stomach where an acid reaction naturally prevails.

It has long been known that the enzyme diastase does not exist in any appreciable quantity in the normal fresh barley seed, but is produced during the life process of germination. Green states that the enzyme of the castor seeds is formed in an analogous way, while Connstein found that germination did not materially increase the enzymic power. In experiments carried on to throw further light upon this point a mechanical difficulty appeared which made it practically impossible to get comparable results between the fresh seeds and the germinated seeds. In the process of germination a chemical change takes place which greatly modifies the properties of the kernel of the seeds, rendering it so pasty and tough that an emulsion with the fat to be hydrolysed is made with great difficulty. Hydrolyses carried on with these imperfectly prepared seeds under optimum conditions gave results not rising above 45 per cent. When, however, the oil was extracted, the residue was a dry, white powder resembling the residue of the fresh seeds but having an

offensive odor. The hydrolytic power as compared with the extracted fresh seeds was, with fresh seeds:—

| Ratio of extract to fat | Time in hours | Per cent. hydrolysis |
|---|---|---|
| 10 : 1 | 48 | 95.4 |
| 10 : 1 | 72 | 97.8 |

With the germinated seeds extracted residue showed on an average:—

| Ratio of extract to fat | Time in hours | Per cent. hydrolysis |
|---|---|---|
| 10 : 1 | 48 | 85.3 |
| 10 : 1 | 72 | 88.6 |

These results indicate that the process of germination decreases rather than increases the hydrolytic principle.

As a result of our work we are of the opinion that the main difficulty in converting this laboratory method into a technical process for the hydrolysis of fats lies in the preparation of a perfect emulsion. As the percentage of fatty acid increases there is a tendency for the emulsion to break, thus diminishing or sometimes practically terminating the reaction. In preparing an emulsion care must be taken not to operate for any length of time above the critical temperature, which lies somewhat below 50° C., and to guard against an excess of water.

In the laboratory we found the difficulties of emulsification to increase rapidly as the amount of material operated upon grew larger, and on account of lack of facilities we were not able to carry out the reaction on the scale desired. We believe, however, that the utilization of this vegetable enzyme is a promising field for further endeavor.

LABORATORY OF INDUSTRIAL CHEMISTRY,
June, 1904.

## *BOOK REVIEWS.*

### Analytical Chemistry.[1]

It is seldom that the reviewer has the privilege of examining two more excellently written and printed volumes than Dr. Treadwell's Qualitative and Quantitative Chemical Analysis as translated by Mr. Hall. The second part of this work on quantitative analysis is of about the same size as the first volume, and it is characterized also by the same clear, concise, and accurate method of statement and arrangement of details which, in the reviewer's opinion, made the first portion especially worthy of praise.

The book is divided into three parts, viz.: 1. Gravimetric Analysis (*a*) metals, (*b*) metalloids, 372 pages. 2. Volumetric Analysis, 148 pages. 3. Gas Analysis, 72 pages. Besides these, there is a short introduction briefly describing methods of manipulation, and the book finishes with some twenty pages of reference tables, logarithms, and chemical conversion factors. The introduction includes, among other things, careful directions for the use of the balance and the calibration of weights, while preceding the volumetric portion an analogous description of methods for determining the accuracy of volumetric measuring instruments is given, and these are so clearly stated and well chosen that they cannot fail to impress upon the student that the foundations for accuracy in chemical work depend as much upon the careful physical control of his tools as upon his own manipulation and understanding of chemical principles.

A summary of the methods included in the book is out of the question within the limits of a review. The analyses are confined, for the main part, to inorganic materials. Details for the determination and separation of the commoner metals and metalloids are given, with reasons for the same. In fact, the explanations for certain procedures,

[1] Analytical Chemistry, Vol. II, by F. P. Treadwell, Ph.D., Professor of Analytical Chemistry in the Polytechnic Institute of Zurich; translated by William T. Hall, S. B., Instructor in Chemistry, Massachusetts Institute of Technology. John Wiley & Sons. 8vo, xii + 654 pages, 96 figures. Cloth, $4.00.

too often obscure, *i. e.*, the use of the old atomic weight of platinum in calculating the amount of potassium in potassium platinic chloride — are one of the features of the book, and cannot fail to be helpful to the student. It is also refreshing to see the Gooch crucible at last duly recognized in a German work. Still, there are many places where the Gooch crucible could be used to advantage where the method of drying on filter paper is recommended, a procedure which, in the opinion of the reviewer, is in almost every instance not only avoidable but best avoided. The greatest fault of the section on assaying is its brevity. It will be highly valuable as side reading in an assaying course for the careful explanations given. No mention is made, however, of the assay-ton system of weights. The volumetric determinations are well chosen, and embody the best and latest applications of acidimetry and alkalimetry, and of oxidation, reduction, and precipitation methods. The section on gas analysis is as full and complete as most instructors will desire, and describes the use of the latest and best forms of apparatus for technical gas analysis.

Throughout the book references to the literature are copiously given, and the authors and modifiers of methods have received due credit therefor. Probable impurities of reagents and methods of purification are carefully pointed out. Calculations of results are given for many typical analyses in a manner that should prove helpful to the student, but are not carried to the extent that requires no use of the reasoning faculties.

The work of the translator has been well done, and he has rendered an excellent German work into good, readable English. He has received efficient aid in the criticism of the proof sheets, for each part has been examined by an expert and shows the results in footnotes of value. In one or two instances the translator has substituted methods or made changes in the original of a far-reaching character. In every instance observed it has been of advantage to the book. It is to be regretted, since American practice is slow to receive recognition abroad, that more changes of this kind were not made. The Wilfarths and Jodlbaurs modifications of the Kjeldahl nitrogen method could be well replaced by the Gunning and the Gunning modified, which are better methods and official in the United States. The method of Pincus, almost never used in actual phosphate control in America, might have been well supplemented by the official volumetric method for phosphates. The mention of the use of the rotary cathode would have improved the electrolytic methods. The Marsh-Berzelius method for small amounts

of arsenic will be sought for and missed by many. Again, it is probable that the retention of Ostwald's theory of indicators may not seem wholly justified by the footnote references to Stieglitz's article on the subject. Criticism can, however, find little foothold in the book, and, in the reviewer's opinion, must rest almost wholly on the differences inherent to foreign practice. Careful investigation might show that practice to be better in many instances, while on the other hand much is to be learned here. That Dr. Treadwell, himself of American parentage, has recognized this fact is evinced by the incorporation of the work of many Americans, and due credit to such well-known chemists as Hillebrand, Blair, Gooch, and others.

Mr. Hall has given us a valuable book for our own and our students' use. It will be much more frequently referred to than Fresenius, Sutton, or Hempel. The publishers have put it into well-arranged form, in clear type, on good paper. It will soon be found in every important laboratory in the country, and to any chemist is well worth the price asked.

CHARLES LATHROP PARSONS.